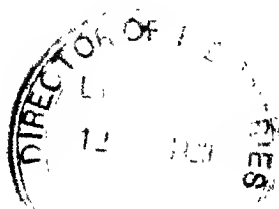




MONOGRAPHS ON INDUSTRIAL CHEMISTRY
EDITED BY SIR EDWARD THORPE, C.B., LL.D., F.R.S.

CEMENT



CEMENT

BY
BERTRAM BLOUNT, F.I.C.

ASSISTED BY
WILLIAM H. WOODCOCK, F.C.S.
MEMB. SOC. PUB. ANAL.

AND
HENRY J. GILLET

WITH DIAGRAMS AND ILLUSTRATIONS

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MONOGRAPHS ON INDUSTRIAL CHEMISTRY

Edited by Sir EDWARD THORPE, C.B., LL.D., F.R.S.

*Emeritus Professor of General Chemistry in the Imperial College of Science and Technology,
South Kensington; and formerly Principal of the Government Laboratory, London.*

INTRODUCTION

DURING the last four or five decades the Applications of Chemistry have experienced an extraordinary development, and there is scarcely an industry that has not benefited, directly or indirectly, from this expansion. Indeed, the Science trenches in greater or less degree upon all departments of human activity. Practically every division of Natural Science has now been linked up with it in the common service of mankind. So ceaseless and rapid is this expansion that the recondite knowledge of one generation becomes a part of the technology of the next. Thus the conceptions, of chemical dynamics of one decade become translated into the current practice of its successor; the doctrines concerning chemical structure and constitution of one period form the basis of large-scale synthetical processes of another; an obscure phenomenon like Catalysis is found to be capable of widespread application in manufacturing operations of the most diverse character.

This series of Monographs will afford illustrations of these and similar facts, and incidentally indicate their bearing on the trend of industrial chemistry in the near future. They will serve to show how fundamental and essential is the relation of principle to practice. They will afford examples of the application of recent knowledge to modern manufacturing procedure. As regards

their scope, it should be stated the books are not intended to cover the whole ground of the technology of the matters to which they relate. They are not concerned with the technical *minutiae* of manufacture except in so far as these may be necessary to elucidate some point of principle. In some cases, where the subjects touch the actual frontiers of progress, knowledge is so very recent and its application so very tentative that both are almost certain to experience profound modification sooner or later. This, of course, is inevitable. But even so such books have more than an ephemeral interest. They are valuable as indicating new and only partially occupied territory; and as illustrating the vast potentiality of fruitful conceptions and the worth of general principles which have shown themselves capable of useful service.

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PREFACE

WHEN I was asked by Sir Edward Thorpe to write one of the series of books which are being published under his Editorship, I hesitated but a short time. The reason for a hesitation, which may be, perhaps, excusable, arose from the fact that the subject is large and difficult, that many able brains and pens have been engaged in its exposition, and I was not sure whether I could add anything of value to the works already published. But the hesitation disappeared as soon as I realised that, on account of the long period which had elapsed since the knowledge of cement was purely empirical, and equally the comparatively small time which has sufficed to place a somewhat crude art on a scientific basis, there might be room for something of the nature of a monograph. My readers will judge in what degree I have been able to fulfil my purpose.

B. B.

76-78 York Street,
London, S.W.
1919.

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INTRODUCTION

THE word cement, although now conveying the definite meaning of a material capable of sticking things together, has an origin less clear than might be supposed at first sight, and a significance in earlier times which is not identical with that now attached to the word. The explanation of the word as given in the *New English Dictionary* will make this clear.

CEMENT.—Middle English, *cymēt*; Old French, *ciment*; Latin, *caementum*, and late Latin, *cimentum*. A contraction for *caedimentum*, meaning rough unhewn stone, the literal meaning being the product of cutting or chipping. The name appears to have been given to broken or pounded stone, tiles, etc., mixed with lime to form a setting mortar, and at length to the mortar or plaster so formed, whence it passed into the sense of strong setting mortar or of mortar generally, however made.

The article in the *New English Dictionary* proceeds thus, the meaning of the word being given under several heads—

“(1) A substance used to bind the stones or bricks of a building firmly together, to cover floors, to form walls, terraces, etc., which being applied in a soft and pasty state, afterwards hardens into a stony consistency; especially a strong mortar, produced by the calcination of a natural or artificial mixture of calcareous and argillaceous matter. Hydraulic cements harden under water and are used for piers, dock walls, etc. Roman cement, like all the hydraulic cements, is an argillaceous lime. Portland Cement is so called because it resembles in colour the Portland stone. It is prepared by calcining a mixture of the clayey mud of the Thames with a proper proportion of chalk (Ure).

“(2) Any substance applied in a soft or glutinous state to the surfaces of solid bodies to make them cohere firmly,” etc.

It will be seen from this that the original word *caedimentum* has nothing to do with *cement* in the sense now generally used. Also that even in this excellent Dictionary cement—that is, something which itself sticks things together—is confused with mortar, which consists partly of cement and partly of some inert material.

In this connection the following passage from Desch, *The Chemistry and Testing of Cement*, may be quoted—

“It is remarkable that the word cement in its late Latin and old French forms was first employed to designate such materials” (viz. ground pottery and the like), “now classed as artificial pozzolanas; its meaning then changed to denote the mortar prepared by mixing the three ingredients, and it is only in recent times that it assumed its modern meaning.”

It will be seen from this that the word Cement has not only a false origin but has been used until lately in the sense, not of cement, but of something containing cement—that is, mortar. In the following pages the word will be used throughout in its modern significance of a material which itself causes other materials to adhere to each other.

Although cements may vary in chemical nature from casein to iron oxide, yet by common consent and because of the enormous practical importance of calcareous cements the term, used without qualification, is restricted to these, and it is of calcareous cements that I propose to treat. There are numerous varieties of these, but they all fall into two groups, (1) the calcium silicate group and (2) the calcium sulphate group. The first is typified by Portland Cement and the second by Plaster of Paris. It must not be supposed that the groups are sharply defined, as the calcium silicate group may contain sulphate in appreciable amount, which, although it may not itself act as a cement, certainly materially influences the behaviour of the cement proper; and, on the other hand, the sulphate group often contains silicates which themselves probably function as cements, besides modifying the behaviour of the calcium sulphate, which is the cementing material proper. This division does not include lime mortar, which is in a class by itself, and must be so, because it may be made from lime so nearly pure that any question of calcium silicate and calcium sulphate disappears, or from lime containing either or both, and in the case of silicate cements may be a lime so siliceous that it comes into the rank of true siliceous cements. It will be seen, in fact, that there is a large range of these materials, and that they are grouped for convenience and not with the notion of establishing a rigid classification.

Little more need be said of the general nature and classes of cements, and it remains to examine the matter in detail.

CEMENT

CHAPTER I

HISTORICAL

IN days almost prehistoric the human race erected very considerable buildings, and as early civilisation was in the East and in relatively dry places they cared little about cement. The natural beginning was to take the local material, whatever that might be, clay, marble, limestone, and the like, and to put it together so that it might make a fairly stable structure. The stability depended on design for materials the surfaces of which were rough enough to resist dislodging stresses. It was soon found by the builders of the period that in order to ensure the stability which they sought the surfaces must not only fit, but also be compelled to adhere the one to the other. Hence it came about that some plastic material was used for this purpose. As all very early buildings were made of dried mud, in a dry climate the natural cement was mud. An improvement came about when the sun-dried bricks of Assyria were cemented together with bitumen. As the adjacent regions are volcanic this substance was fairly easily procurable, and could be well used now, as it is an excellent material, if modern conditions had not put it to other and more specialised purposes.

The next step seems to have been the use of a calcareous material cementing together pieces of the local stone. It may happen that the stone and the cement are of similar composition, and that the only substantial difference between them is that the latter has been prepared by burning. For example, the calcareous stone forming the rock from which the Great Pyramid is constructed is a crude gypsum, and the mortar used in cementing the blocks is the same substance burnt. As the countries in which this kind of cement originated are almost destitute of fuel and have but little need for it, the natural

conclusion is that the discovery was as empirical as that of glass. Some unknown pioneer found that when calcareous stones were burnt they differed from the original stone, were softer, were easily ground, and when mixed with water would set. It seems fairly certain that, from the time when sun-dried mud bricks were cemented together with mud and made dwellings not unlike the adobe dwellings of to-day in tropical America, in that dried mud is the principal constituent of both, the one thing sought was an adhesive material which would stand the local conditions. To illustrate these points a passage from Dr. Desch's book may be quoted---

"In the massive masonry constructions of the Egyptians we meet with our present-day system of uniting blocks and slabs of stone with a mortar consisting of calcareous adhesive material. There is some little uncertainty as to the character of this material. Whilst it is generally described by writers on Egypt as burnt lime, even when found in buildings as old as the Great Pyramid, the statement is definitely made that the Egyptians never used lime, and that the cementing material was always obtained by burning gypsum. As the gypsum was quarried in a very impure state, it usually contained calcium carbonate, which might be partly decomposed in the process of burning, or even if found in an undecomposed state in the mortar would produce the impression that lime had been used."

Taking these facts into account, it is fairly clear that at that early date calcareous materials *were* burnt and that they were used indiscriminately, whether of the sulphate or siliceous class. It is no reflection on ancient architects to say that their cemented structures would have perished had not the climate been very dry. It is generally admitted that the climate of Egypt has changed since the erection of the Assouan Dam, and that rain is less rare. Accepting this, cement suitable at 2000 B.C. would not be suitable now.

There was a gap between these ancient times and that of the Romans which is not well bridged, but it may be reasonably assumed that as civilisation spread from the near East, and with it the arts of the architect and builder, the need for a local material sufficiently resistant to the weather conditions of more westerly countries became urgent, and that a plastic material less susceptible than clay to the action of water had to be adopted. Lime by itself when slaked is admirably plastic

when mixed with a further quantity of water, but on drying shrinks and needs some sort of inert filling material in order to make a mortar which will keep its volume approximately constant. The material sufficiently fine in grain and wide in distribution is sand; hence lime mortar as used from a date unknown to the present day.

It is doubtful whether any clear knowledge existed then as to the reason why some lime was better than others, and the merit of each was indicated by its place of origin, much as Buxton lime and Dorking lime are distinguished now, although it would puzzle the average user to state the cause of difference, a sufficient indication of the neglect of education in natural science concerning things of everyday life and couched in such simple language that any intelligent child can understand.

The Romans understood calcareous cements exceedingly well, as their structures testify, and they were probably the first people deliberately to make hydraulic cement. Ordinary lime mortar, no doubt, was used, but a true hydraulic cement was prepared by adding puzzolanic material, *i. e.* a substance containing siliceous matter sufficiently active to combine with lime to form calcium silicates resistant to the action of water. The nature of the substances mentioned, together with their chemical composition, will be given in a later chapter.

The decay of civilisation which followed the destruction of the Roman Empire had as one of its results the decline of the art of the builder as far as one essential part, *viz.* mortar-making, was concerned. In the Middle Ages empiricism reigned supreme in all directions, and mortar was made from limestones which had a local reputation based on the belief or prejudice of the local user. Fortunately, as limestones are often siliceous, a good range of hydraulic materials was available, and as puzzolanic materials, though not common, occur in a fair number of places, and as ground-up brick rubbish forms a good substitute for such materials, hydraulic cement could be prepared, though in such a casual and ignorant manner that the failures of structures intended to resist the action of water must have been many—how large a proportion it is impossible to say, as their destruction removed the evidence of their existence.

The situation remained unaltered until the time of Smeaton, who in 1756 was commissioned to replace the earlier Eddystone Lighthouse which had been burnt. An account of his experiments on the cement to be used is included in his story of the whole

undertaking, published some years later. The facts recorded seemed to me so interesting that I quoted them in a lecture which I delivered to the Institute of Chemistry in 1912, and now give the whole extract, together with my own introductory words.

“ I do not find any record that limestones were deliberately and intelligently chosen for the hydraulic quality of the lime which they furnish until the time of Smeaton, who, in considering with what material he should build the Eddystone Lighthouse, ascertained that Aberthaw limestone (a blue lias formation) was undoubtedly hydraulic, and, desiring to know why, applied to Mr. Cookworthy, a chemist of the period, whose office as a consultant was creditably fulfilled. It was found that those limestones which were most hydraulic contained the largest proportion of argillaceous matter. But not content with this, he reasoned that this quality might be improved by the addition of what was then known to be capable of conferring hydraulic properties on ordinary lime, and accordingly used Trass. In Smeaton's own words—

“ In this respite from sea operations, I seriously began to consider the great importance that it was likely to be of to our work, to have a Cement the most perfect that was possible, to resist the extreme violence of the sea. And on consideration of this matter, it appeared, that nothing of the resinous, or oily kind, could have any place in our work, as it would require the surface to be dry, to enable it to make a compleat adhesion; whereas the getting anything compleatly dry, was one of our greatest difficulties. It seemed, therefore, that nothing in the way of Cement would answer our end, but what would adhere to a moist surface, and become hard, without ever becoming compleatly dry.

“ I began now to foresee that before I could have a compleat sample produced of every part of the work, that might be wanted for the operations of next season, it would be pretty far advanced in the spring; and as I proposed beginning the outwork as early in the season as possible, I determined to winter at Plymouth (without returning to my residence in London, as I had before intended) though to the detriment of my own private concerns; laying every consideration aside in favour of the Eddystone. I therefore resolved to take every opportunity in the evenings and intervals of my attendance on the work-yard, mould-room, etc., to go through a compleat set of experiments on Cement,

so far as it concerned the subject I had in hand; for I plainly saw from the manner of working the moorstone, already described, that not only much of the beauty and neatness of the work, but its real solidity too, would depend upon getting a cement that would, in spite of water almost continually driven against it with every degree of violence, become so firm a consistence in itself, and adhesion to the stone, that it should lie fair and flush in the joints, and so as to compose one even regular surface with the stone; and without needing hoops of iron or copper to surround the horizontal joints, as seems to have been the expedient of Mr. Winstanley. I was fortunate to succeed in this part of the business entirely to my satisfaction; and perhaps in a degree unknown before; and having made much use since of the experience which I then acquired; having had frequent occasions and opportunities of communicating it to others, and having been asked many questions concerning it; I trust that my reader will forgive me, if I am diffuse enough to enter into a full explanation of the subject, so far as I know it. I mean not however to tire him with recording all the particular experiments, as this would be almost endless, they having been pursued through the whole of this winter; but only to state the principal scope and design of them, with the results; nor do I propose to enter into a chemical disquisition upon them, which I leave to the learned in that science. But as what I have to say on this subject will carry me to some length I shall reserve it to a distinct chapter, in order to keep the matter together.

“On this subject I was already apprised that two measures of quenched or slaked lime, in the dry powder, mixed with one measure of Dutch Tarras, and both very well beat together to the consistence of a paste, using as little water as possible, was the common composition, generally used in the construction of the best water-works both in stone and brick, and which, after being once set,¹ would afterwards become hard, without ever being completely dry; nay, that it would in time grow hard, even under water. This therefore seemed to be the kind of cement adapted to our use.

“Having heard of a lime produced from a stone found at Aberthaw, upon the coast of Glamorganshire, that had the same qualities of setting in water as Tarras, I was very anxious to

¹ “This is the term used in the application of calcareous mortar, which denotes its first step, or degree of hardening; but in this state, though it has lost its ductility, it is a very friable substance.”

procure some of the stone, which I did, and burnt it into lime. I found it to require a good deal of fire to make it, by quenching, fall into a fine powder. This stone, before burning, was of a very even, but dead sky blue, with very few shining particles; but when burnt and sifted, it was of a bright buff colour. Having made up a couple of balls, according to each of the former proportions; and also a couple of balls with common lime (by which I mean Plymouth lime) the difference of hardness after twenty-four hours was very remarkable: the composition of Aberthaw to one of Tarras considerably exceeded in hardness that of common lime and Tarras in equal parts; the composition of Aberthaw and Tarras in equal parts was still considerably harder, and this difference was the more apparent the longer the compositions were kept.

“ Having now found a species of materials, and a method of compounding them very competent to our purpose; and having plainly seen that there was a great difference in the effect, arising from the different nature of lime burnt from different kinds of limestone; and that its acquisition of hardness under water did not depend upon the hardness of the stone; inasmuch as chalk lime appeared to be as good as that burnt from Plymouth marble; and that Aberthaw lime was greatly superior to either for the purpose of aquatic buildings, though scarcely so hard as Plymouth marble; I was very desirous to get some light into some of the sensible qualities, that might probably occasion the difference, or at least become a mark of distinction. I therefore applied to my friend Mr. Cookworthy, whom I had found at all times ready to afford me his assistance, wherever his knowledge could be of use to me. He taught me how to analyse limestones: and though my chemical friends will be at no loss upon this subject; yet as it is very possibly that some of my readers may be no more acquainted with chemistry than myself; for the sake of these I will describe the process, as being useful for all those who are concerned in building to know.

“ I took about the quantity of five penny weights (or a guinea's weight) of the limestone to be tried, bruised to a coarse powder; upon which I poured common aqua fortis, but not so much at a time as to occasion the effervescence to overtop the glass vessel in which the limestone was put; and added fresh aqua fortis after the effervescence of the former quantity had ceased, till no further ebullition appeared, by any addition of

the acid. This done, and the whole being left to settle, the liquor will generally acquire a tinge of some transparent colour; and if from the solution little or no sediment drops, it may be accounted a pure limestone (which is generally the case with white chalk and several others) as containing no uncalcareous matter; but if from the solution a quantity of matter is deposited in the form of mud, this indicates a quantity of uncalcareous matter in its composition. When this is well settled, pour off the water, and repeatedly add water in the same way, stirring it and letting it settle till it becomes tasteless. After this let the mud be well stirred into the water, and without giving it time to settle, pour off the muddy water into another vessel; and if there is any sand or gritty matter left behind (as will frequently be the case) this collection by itself will ascertain the quantity and species of sabulous matter that entered into the texture of the limestone. Letting now the muddy liquor settle, and, pouring off the water till no more can be got without an admixture of mud, leave the rest to dry; which, when it comes to the consistence of clay, or paste, make it into a ball and dry it for further examination.

“From the experiments now related, I was convinced that the most pure limestone was not the best for making mortar, especially for building in water: and this brought to my mind a maxim I had learnt from workmen; that the best lime for the Land was seldom the best for Building purposes; of which the reason now appeared; which was, that the most pure lime affording the greatest quantity of Lime Salts, or impregnation, would best answer the purposes of Agriculture: whereas, for some reason or other, when a limestone is intimately mixed with a proportion of Clay, which by burning is converted into Brick, it is made to act more strongly as a Cement.¹ This suggested to me the idea, that an admixture of clay in the composition of limestone, when treated as above specified, might be the most certain index of the validity of a limestone for Aquatic Buildings: nor has any experience since

¹ “It is not to be wondered at, that workmen generally prefer the more pure limes for building in the Air, because being unmixed with any uncalcareous matter, they fall into the finest powder and make the finest paste, which will, of course, receive the greatest quantity of Sand (generally the cheaper material) into its composition, without losing its toughness beyond a certain degree, and requires the least labour to bring it to the desired consistence; hence mortar made of such lime is the least expensive, and in dry work the difference of hardness, compared with others, is less apparent.”

CEMENT

contradicted it; as all the limestones in repute for water-works, that I have met with, have afforded this mark; even the Dorking lime much esteemed for these uses at London, and in the country round about, is plainly nothing but a species of chalk, impregnated with clay, of which it makes one full seventeenth part of the original weight.'"

It will be seen from this that even as late as the middle of the eighteenth century the only mode then known of deciding on the suitability of calcareous cements for any given purpose was by their local celebrity. Smeaton had heard of the reputation of Aberthaw lime. The deposit of Blue Lias limestone runs through this country, and its south-west end occurs in South Wales and Lyne Regis. It is always intercalated with layers of calcareous shale, and is an excellent cement-making material when suitably mixed with its neighbouring deposits. But at the time when Smeaton worked this was not known, and "Aberthaw limestone" meant the pieces of stone washed down from the cliffs lying about on the foreshore. To this day they are collected at Lyne Regis and are sent to South Wales to be burnt. Smeaton had also heard of "tarras," now called trass, and believed it to be Dutch, because it reached this country from Holland. But trass is a product evidently of long-ago volcanic origin which came from Andernach on the Rhine, and as known not by its country of origin but by its country of exportation. At the date when Smeaton was most active scientific knowledge was not at its best. The virtuosi of 1670 were dead, but had left their mark; the literary crew of "Great Anna whom three realms obey" reigned supreme; the renaissance of science had yet to come, and in his own corner of science Smeaton did work which is as permanent as his lighthouse as stable.

In chronological order the next step was the production of the real forerunner of Portland cement, when, about the end of the eighteenth century, it was found that certain lumps of stony material dredged up from certain localities would, when burnt, yield a cement. These materials are mentioned in a later chapter. They were named Sceptaria Nodules, which is a purely geological term meaning masses of material which have been naturally separated from their matrix. These conglomerate masses consist of argillaceous and calcareous materials in suitable proportions for the making of hydraulic cement when they

are burnt. This interesting and useful fact was discovered quite empirically, and an industry was started. It happens that these "septaria nodules" contain both iron and manganese, and that on this account they yield, when burnt, a reddish cement. As Roman cement, properly so-called, consists of lime and puzzolana (which may be red), or ground tiles, the colour of the material led to the use of the name Roman cement as a mode of description. Of course, there is no connection between the two things, true Roman cement being a mixture of lime with puzzolana and the material made here by burning septaria nodules being an inferior variety of Portland cement. As in this country the use of puzzolanic cements had been neglected, and local limes more or less hydraulic had been employed with rather chancey results, it can be understood that the advent of a true hydraulic cement ground and ready to mix with water was hailed with acclamation, and a large and profitable trade sprang up. There is no question but that Roman cement is an admirable material and perfectly resistant to water, but on account of its chemical composition, which is dealt with in a later chapter, it is inconveniently quick-setting. Yet such are its merits and vogue that it was in use for setting what are known as "squares" in the Yorkshire system of brewing beer. "Squares" are large tanks made of Yorkshire flags, and are tongued and grooved to make a beer-tight joint. The mason's work is usually good, but a cement is necessary to complete the joint. The cement generally used some twenty years ago was Roman cement—quite the most inappropriate material which could be chosen, as it sets quickly, and the slabs of stone which make the vat are large and heavy, and must be lowered exactly to their places by ordinary slow-moving tackle and must be adjusted with the utmost nicety in order to make a proper joint. I remember a case of the kind where Roman cement was used for this purpose and failed lamentably, not at all because of bad quality, but because it had half set before the slabs were got into position. Of course, good hydraulic lime should have been used, but as the builders of these vats had been using Roman cement for years, from father to son, so to speak, they would have repudiated hydraulic cement as likely to spoil the beer.

Apropos of this, and to show how completely empiricism has been replaced by scientific knowledge, it is a fact that in the early days of the tube railway the grouting outside the tubes was made with hydraulic lime, which was preferred to Portland

cement because of its slow setting, so that if a small settlement took place the cement would shift slightly and still protect the cast-iron tube from the soil surrounding it.

In 1827 an English bricklayer named Aspdin stumbled on the fact that a mixture of chalk and clay, when burned, produced hydraulic cement, and proceeded to manufacture it on a small scale. At that date the cement had a composition not far removed from that of Roman cement, though with a somewhat higher percentage of lime, say 55 % as against 45 % for Roman cement. The burning process was of the roughest description, and parts of the charge, burnt in common lime-kilns, were overheated, and other parts half burnt. So complete was the ignorance of the time that the under-burnt stuff was preferred to the harder masses, which were true clinker. This notion that material which has been hard burnt is useless as cement held its own not only in this country, but in France, where the nodules, called "grappiers," obtained in the process of making *chaux de Teil* were rejected and the lime alone used, until some one found that when ground finely they yielded a cement much superior to the Teil lime, which itself is famous as an hydraulic cement. This foolish idea persisted generally in this country for many years, and the writer has heard venerable persons solemnly discussing the best way of getting rid of the evil over-burnt material. There was some excuse for this singularly unscientific attitude, as in one respect a half-burnt friable product is preferable to one properly clinkered, in that it is easier to grind, especially with the crude grinding apparatus, such as millstones, in use thirty years ago.

In the early days of the manufacture of Portland cement, burning was so irregular that those makers, who were careful of their product, and understood that hard well-burnt clinker was what they should prepare for sale, made a practice of picking from the material, unloaded from the kilns of that date, all under-burnt portions.

This was a considerable advance on the older practice of putting everything crushable, including any old firebrick which had been detached from the kilns during the process of burning, into the mills.

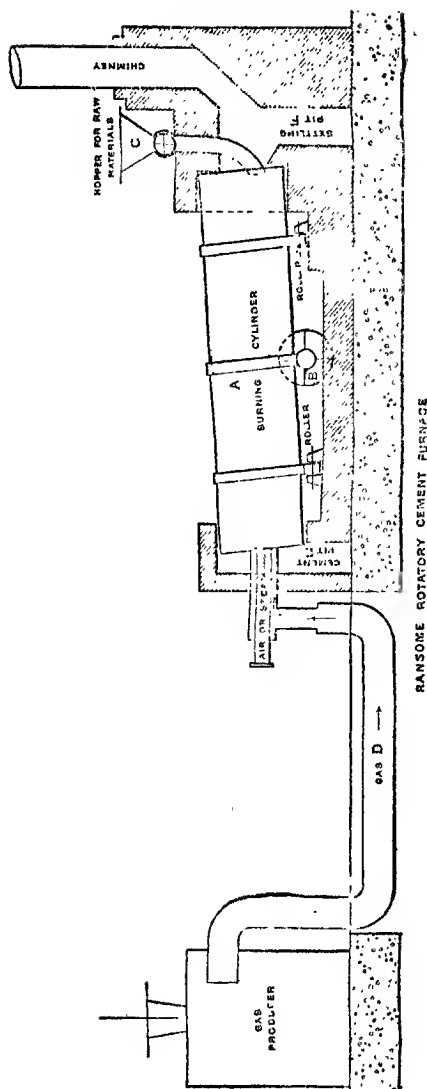
The next stage in the history of Portland cement was the introduction of the rotatory kiln. This history is given in a paper read before the Institution of Civil Engineers by my late partner and myself in 1901, and it is convenient to quote from

this as a record of the knowledge of the time. I have great pleasure in acknowledging the permission given to me by the Institution of Civil Engineers to publish the following quotation—

“In 1877 Thomas Russell Crampton, M.Inst.C.E., patented a process for burning cement in rotatory kilns, but appears not to have put his invention on a manufacturing footing. It may be accepted that the earliest form of rotatory kiln which approached practical success was invented in this country by the late Mr. Frederick Ransome, Assoc.Inst.C.E.; this kiln may be regarded as the forerunner of modern rotatory kilns now being erected or at work in England or abroad. Ransome's English patent is dated May 2, 1885, and in view of the subsequent development of the rotatory process, affords an interesting object of study.

“The Ransome kiln shown in Fig. 1 consists of a cylindrical furnace A, set at a slight inclination, carried on rollers, and rotated by worm-gearing B. At the upper end powdered raw material is fed in by the hopper C, and travels down the furnace, meeting burning producer-gas entering by the pipe D. The burnt material falls into the pit E, and any raw material which may be blown back up the furnace is caught in the settling-pit F, whence it can be returned to the hopper.

“The inventor states that whereas in ordinary methods of burning cement it has always been necessary ‘to grind the cement after burning to bring it to the requisite degree of fineness,’ in his process ‘by introducing the cement material into the rotating chamber as a fine powder the necessity for grinding the cement after burning is entirely obviated.’ This idea, which is put forward in his provisional specification, is emphasised in the complete specification, where the following passage occurs: ‘The slurry is dried, then pulverised, and afterwards sifted to bring it to the degree of fineness required in the sifted cement, so that the cement produced may be used without subsequent grinding.’ It is abundantly evident that one of the chief objects which Mr. Ransome had in view was the abolition of the costly process of grinding clinker. His claim to accomplish this was made in ignorance of the fact that at the temperature necessary for burning Portland cement the material becomes plastic and sticky, and although it may be in the finest powder before burning, yet it will cohere and form small nodules or lumps when burnt. He also failed to see that



systematic heating of the raw material by passing it through the kiln in a direction opposite to that of the burning gases was of fundamental importance, because he suggests introducing the raw material at the end where the burner is situated, as an alternative to the correct and rational method of feeding it in at the end remote from the burner. But although in error in these two important respects, the inventor saw clearly that a great saving in the cost of production (largely due to economy in labour) would be effected by a rotatory process, and that the cement made by such a process would be more uniformly burnt than that made in masses in a fixed kiln."

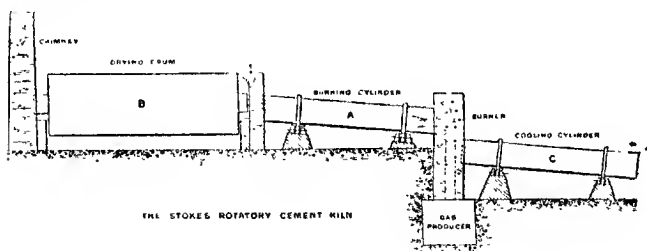


FIG. 2.

"A substantial improvement on the Ransome apparatus was made by Mr. Wilfrid Stokes, who realised clearly that one of the merits of a properly contrived rotatory process is the economical and systematic use of heat."

"In the Stokes process precautions were taken to effect a considerable economy in fuel. The whole apparatus was particularly well thought out, and its failure to realise the expectations of its inventor is greatly to be regretted, the more so as it delayed for nearly ten years a much-needed improvement in an important industry, and allowed the centre of interest to shift from this country, which is the birthplace of the rotatory process, to the United States, which is its country by adoption, and where it has developed and prospered. The plant is shown in Fig. 2. A is the burning-cylinder about 35 ft. long and 5 ft. in diameter, constructed of steel plates and mounted on two sets of live rollers resting on a cast-iron cradle, with freedom to allow for expansion and contraction. The cylinder is driven by a small engine and spur-gearing; it is lined with refractory bricks. The waste gases from the burning-cylinder pass through

the drying-drum B about 40 ft. long and 12 ft. in diameter. At each end of the drum is a roller-path resting on supporting wheels, and the drum is slowly rotated by worm-gearing driven by a small engine. The slurry is fed on to the outside of the drum by means of a dipping arrangement which delivers a definite quantity of slurry from a long trough (not shown in the figure) above the drum. The slurry adheres to the drum and is dried by the time the drum has nearly completed a revolution,

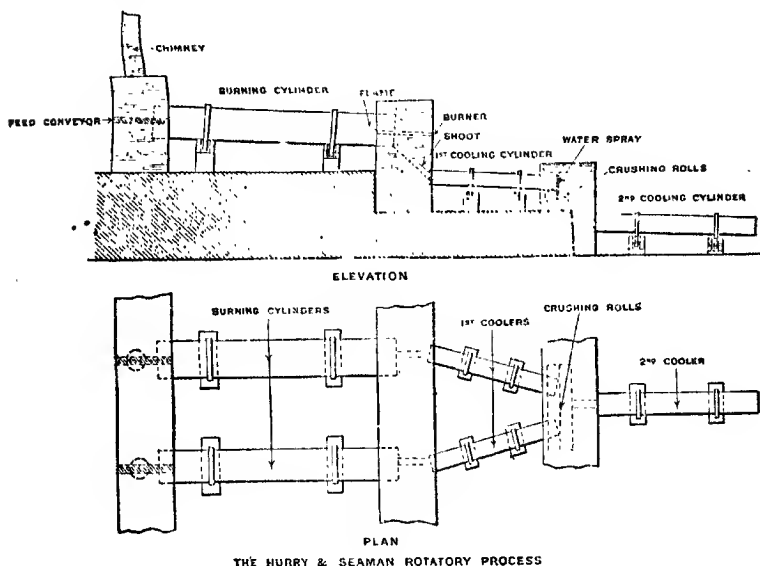


FIG. 3.

when it is scraped off by a series of chain scrapers driven along the top of the drum and delivered into the feed-shoot of the burning-cylinder. The clinker emerging from the lower end of the burning-cylinder falls into the cooling-cylinder C, 35 ft. long and 5 ft. in diameter. This cooling-cylinder is of steel, unlined but provided with gills which aid in abstracting heat from the clinker to be cooled. The drying-drum, burning-cylinder, and cooler are arranged so that the material passes down the series by gravity. The burning-cylinder is heated by gas from a producer; the necessary air is supplied through the

cooling-cylinder, the heat from the out-going clinker being thus regenerated."

The idea of a rotatory process of manufacturing cement had, taken root in the United States, and attempts were made to give it a practical shape by various inventors. One great advantage was the possession of cheap and abundant oil fuel, and the serious difficulties attending the use of producer gas were thus avoided. The next step was to use powdered coal as a fuel to make a sort of blowpipe flame much like that produced by a jet of oil, and this was successfully accomplished about 1896 by Hurry & Seaman at the Atlas Company's works at Northampton, Pennsylvania, which the author visited and reported on in 1898. A drawing of the plant is appended (Fig. 3). Brains were at work on the Continent about the same time, and gradually the modern form of rotatory kiln was evolved. It differs in no essential respect from the earlier patterns, the alterations which have been made being only in the direction of greater size and greater simplicity, especially as regards the burner, which is now usually run, not by an injector as in the Hurry & Seaman system, but by a fan at comparatively low pressure.

From 1900 onwards the rotatory system of burning has had full sway, and at the moment there is little prospect of it being displaced, until what the author believes to be the ultimate goal of the industry, namely, the manufacture of Portland cement by blast-furnace methods, is achieved.

The historical part of this book has been purposely restricted to the recording of the genesis and growth of the industry itself. It is thought that discussion of the gradual improvement of the product and the means by which this has been attained may be better postponed until materials and methods of manufacture and testing have been dealt with in turn.

In the foregoing pages an attempt has been made to construct a coherent narrative of the origin and development of cements, but it is not to be regarded as exhaustive. The historian of such a highly important manufacture has yet to appear, and I do not propose to try to anticipate his labours, which must be as much antiquarian as chemical; but meantime the reader is referred not only to Desch, but to Redgrave, whose book on *Calcareous Cements* contains in its opening chapters many references to matters of historic interest, and to a paper by the same author and Major-General Scott read before the Institution of Civil Engineers in 1880.

CHAPTER II

RAW MATERIALS

FROM the fact that the bulk of the earth's crust consists of acid oxides, and that carbonates of lime, though less common, exist in colossal quantities, it may well be supposed that Portland cement, consisting of basic silicates and aluminates, can be manufactured in many parts of the globe. It is therefore interesting to note how slow was the growth of the industry. The explanation is to be found in the ignorance and prejudices of the majority of architects, engineers and builders, and the casual and empirical mode of manufacture in the early days, which led to the production not only of material poor and uncertain in quality but positively dangerous to use, because its chemical instability causes its expansion when in the work to such a degree as sometimes to destroy the structure. There was another reason of equal importance, namely, the existence of deposits in this country of chalk and clay so abundant and excellent in quality that they were looked upon as a sort of standard raw material, and less amenable substances such as limestone and shale were regarded as of secondary importance. But the amount of true chalk in the world is relatively small. It is found in the south-east part of England, across the Channel in the part of France immediately opposite, and in the northern part of Denmark. As far as I am aware, these are the only deposits of importance on the face of the globe.

It will be easily understood that there are many varieties of calcium carbonate which border on what is generally called white chalk, but are not, as that is almost pure CaCO_3 , and so soft that it can be made into a slurry by mere washing with water, with so little mechanical force that it can be rubbed down to a paste between the fingers. The variant nearest to white chalk is grey chalk, which contains a certain amount of clayey matter. This and examples of all the chief raw materials used for making Portland cement and other types

treated of in this book are collected in this chapter under groups as far as classification is practicable.

These records are admittedly incomplete, but may be regarded as representative of the class of material which may be usefully employed in the manufacture of cement.

It will be seen that the range is very large and that the old notion that cement can be made only at particular places is exploded, but that notion held long enough to cause much injury to the industry, purely for want of technical knowledge.

It is not more than thirty years ago when an eminent cement maker said to the author, quite seriously, that there was no chemical reaction between the chalk and the clay which he used; he added, "Cement is made in the wash mill," and in that respect was right, because a bad mix would obviously make a bad cement; but as to what happened in the kiln he had no idea, and regarded it as part of a ceremony rather than the essence of the process.

For convenience the raw materials are divided into groups according to their nature and not according to their country of origin.

MEDWAY DISTRICT

Chalk	White Chalk.	Grey Chalk.	
Silica	1.36	5.63	3.82
Insoluble }	0.20	0.53	0.40
Ferric Oxide and Alumina {	0.18		4.00
Lime	42.92	41.35	50.56
Magnesia	0.42	0.30	0.72
Sulphuric Anhydride	Trace	Trace	Trace
Carbonic Anhydride	35.30	32.96	40.50
Water	19.03	17.39	
Alkalies and loss	0.53	1.84	
	100.00	100.00	100.00

Only three examples, two of grey chalk and one of white, are given, but they may be regarded as typical. The deposits of both varieties are sufficiently uniform to make them as easy to work, so as to obtain a uniform mix, as any material, the one considerable factor of doubt being the fluctuating quantity of water according to the weather. A normal figure of about 20 % to 25 % for white chalk is quite sufficient to allow the

chalk to be beaten to a paste without the addition of extraneous water, and it can easily be understood how readily such a material can be turned into slurry in the wash mill.

Although not strictly in order, I here insert the substance of a communication which I have received from a cement maker whose experience is both extensive and fully up to date. He deals with the question, as a whole, of the raw materials in use on the Thames, giving figures for all three, viz. chalk, clay and fuel. The figures for chalk can be compared with those given above, and the others with those set forth in later sections of this book.

My informant, Mr. C. W. Sharrock, to whom I tender my best thanks, says: "The average analysis of chalk is over a period of twelve years and covers some hundreds of tests. The composition is wonderfully uniform, the most variable item being water, which in the summer is round about 20 % and in the winter gets up to 24 %."

The analysis given for the chalk is as follows—

Silica	0.40 %
Alumina and Ferric Oxide	0.19 "
Lime	55.01 "
Magnesia	0.64 "
Sulphuric Anhydride	0.29 "
Carbonic Anhydride	43.01 "
Alkalies	0.46 "
	<hr/>
	100.00

These figures represent the composition of the dry chalk. The average percentage of water in the chalk was found to be 22.04 %.

Similarly, the analysis of Medway clay given below represents an average of many hundreds of tests over a period of twelve or fourteen years. To use my informant's own words: "I have found the composition of the material generally uniform, the chief variation being in the water content, but where grab clay is taken there is very little variation. Occasionally, when hand-dug clay is used, or even machine-dug clay, where they are just breaking a new surface we sometimes get an excess of fine silica and water, due to a deposit in what are locally known as 'rillways,' or channels formed on the upper surface of the clay, but these are only exceptional and do not call for serious consideration."

The average analysis referred to is as follows—

Silica	57'02
Ferric Oxide	6'64
Alumina	16'20
Lime	3'27
Magnesia	2'62
Sulphuric Anhydride	0'07
Alkalies	1'00
Iron Pyrites	1'93
Combined water and loss	10'65
	<hr/> 100'00 <hr/>

This is the composition of the dried clay. The average percentage of water in the clay as dug is 44'8 %.

In the case of coal (which may be conveniently included here) three typical analyses—(1) "Ryhope," (2) "Silksworth," (3) An average Midland Coal—have been given me, and my correspondent makes a remark which appears to me very cogent. Thirteen years ago "Ryhope" coal was regarded as the only coal to use, it being very low in moisture, fairly high in volatile matter, and very uniform in quality. The next coal approximating to "Ryhope" was "Silksworth," and the opinion then prevailed that these were the only safe coals to use. On this account the prices of these coals were raised excessively, a fact which led my informant to try other sources. His experiments, made on a practical manufacturing scale, convinced him that this claim could not be sustained. He adds: "The sum total of my experience is that any coal, approximating to the average analysis I have given you of Midland coal, is quite suitable and safe to use; and if the price is anywhere in the neighbourhood of 15 % below that of 'Ryhope' or 'Silksworth,' it is the most economical." I may add that from my own experience I agree entirely with this statement.

The analyses referred to are stated below—

	"Ryhope "	"Silksworth."	Average Midland.
Vol. matter	28'77	26'51	29'56
Fixed Carbon	59'92	63'95	57'73
Ash	11'31	9'54	12'71
	<hr/> 100'00 <hr/>	<hr/> 100'00 <hr/>	<hr/> 100'00 <hr/>
Moisture	2'09	2'14	8'75
Cal. Val. (Cal. per kilo)	—	7639	7117
B.Th.U.	—	13750	12810
Evap. power (lbs. of water at 100° C.)	—	14'25	13'26

Although not strictly in place in this book, yet these figures are so informative and are so well marshalled and commented on by Mr. Sharrock, that I have preferred not to separate them and relegate each of the raw materials to its own section. Other figures, many of them my own, are set forth below—

BRITISH ISLES

Limestones	Buxton	N Wales.	S Wales	N England	N Ireland.	
Silica)						
Insoluble)	0'40	1'14	13'88	1'00	0'36	0'56
Ferric Oxide)						
Alumina)	0'06	0'41	2'60	1'10	0'20	0'12
Lime	55'60	51'84	45'57	51'30	55'52	55'10
Magnesia	0'26	0'26	0'52	0'73	0'20	0'27
Sulphuric Anhydride	Trace	0'00	Trace	—	0'11	0'16
Carbonic Anhydride	43'02	43'26	37'40	42'81	43'52	42'72
Water	0'08	—	—	—	0'08	0'08
Alkalies and loss	—	—	—	—	—	0'09
	100'02	100'00	99'97	100'00	100'02	100'00

Limestones	Oxfordshire				Ireland.	
Silica	2'56	1'22	0'48	3'74	11'78	9'07
Insoluble	0'04	0'66	0'52	21'94	—	—
Ferric Oxide)						
Alumina)	1'50	1'04	1'06	1'80	3'26	2'20
Lime	52'72	53'62	54'36	39'52	42'81	48'10
Magnesia	0'47	0'44	0'61	0'45	2'76	0'80
Sulphuric Anhydride	Trace	0'12	Nil	0'18	—	—
Carbonic Anhydride	41'42	42'26	42'60	31'36	38'00	38'38
Water	0'68	0'66	0'40	0'98	—	—
Alkalies and loss	—	—	—	—	1'39	1'35
	99'99	100'02	100'03	99'97	100'00	100'00

Buxton limestone is one of the purest in the world, and therefore used chiefly for making lime for chemical use. It may be supposed on this ground that but little interest has been taken in cement manufacture in the Buxton region.

There is an example about equally pure from North Wales which is used for chemical purposes and for blast furnaces, but also very largely for cement, and one of a totally different character from South Wales which requires but a small addition

argillaceous matter to make a cement. There are other excellent samples of almost pure limestone from Oxfordshire, the North of England, the North of Ireland, and several others which are more or less siliceous. It must not be supposed that this is necessarily a disadvantage. If the proportion and quality of the siliceous matter are suitable there will be less CO_2 to drive off, and the amount of material handled will be materially decreased.

The comments on these analyses apply to most of the others classified according to the countries from which they were sent to me. Details of the part of the country of origin from which they come are not always available, but for the present purpose it is sufficient to record the large range of composition of limestones suitable for cement making distributed from S. America to Siam and from Russia to S. Africa.

Russia				Sweden.		
Silica						
Insoluble	0.20	0.50	1.34	15.98	2.76	0.54
Ferric Oxide				0.21	—	—
Alumina	0.52	0.28	0.40	6.03	0.76	0.10
Lime	55.00	55.10	51.00	40.86	53.54	55.29
Magnesia	0.53	0.50	0.65	1.12	0.50	0.24
Sulphuric Anhydride	Trace	0.19	0.26	0.50	Trace	Trace
Carbonic Anhydride	43.76	43.40	42.80	32.10	41.28	41.52
Water	0.06	0.03	0.55	2.13	1.17	2.29
Alkalies and loss	—	—	—	0.14	—	—
	100.07	100.00	100.00	100.00	100.01	99.98

Portugal.		S. America.				
Silica						
Insoluble	18.01	5.66	8.67	0.30	5.98	0.40
Ferric Oxide	7.60	3.14				
Alumina	2.96	1.85	0.56	0.34	0.67	0.48
Lime	35.16	46.31	50.59	53.12	50.76	55.08
Magnesia	1.25	1.11	2.00	2.37	1.24	0.38
Sulphuric Anhydride	1.49	2.19	Trace	Trace	Trace	0.03
Carbonic Anhydride	—	—	37.36	43.84	40.40	43.60
Water	32.03	39.28	0.22	Nil	1.01	—
Alkalies and loss	1.50	0.43	—	—	—	0.03
	100.00	100.00	100.00	99.97	100.06	100.00

	Westphalia.		Norway.	W. Indies.	S. Africa.	
Silica and Insoluble	13'20	4'08	25'84	0'76	21'74	10'70
Ferric Oxide . . .	1'82	0'88	6'84	0'60	5'52	3'76
Alumina	4'56	1'74				
Lime	43'14	51'37	34'80	46'39	46'00	51'56
Magnesia	0'81	0'43	2'45	7'71	0'80	0'52
Sulphuric Anhydride	0'01	0'08	Trace	Trace	—	—
Carbonic Anhydride	34'10	40'28				
Water	2'24	1'14	30'07	44'51	25'10	33'44
Alkalies and loss . .	0'12	—	—	—	0'84	0'02
	100'00	100'00	100'00	100'00	100'00	100'00

	Egypt.	India.		France
Silica and Insoluble . .	7'35	1'12	2'51	0'55
Ferric Oxide	0'76			
Alumina	0'99	0'40	1'17	0'20
Lime	50'15	51'10	53'18	54'07
Magnesia	0'72	0'05	0'42	0'51
Sulphuric Anhydride . .	0'21	Trace	Trace	Trace
Carbonic Anhydride . .	39'28			
Water	0'51	43'34	42'72	43'77
	100'00	100'00	100'00	100'00

	Jamaica	Spain.
Silica and Insoluble . . .	0'20	0'44
Ferric Oxide		
Alumina	0'08	0'12
Lime	56'02	54'00
Magnesia	0'24	0'95
Sulphuric Anhydride . . .	Trace	Trace
Carbonic Anhydride . . .	43'28	43'00
Water	0'18	—
	100'00	100'01

Before leaving the question of raw materials of the limestone class a word may be said of a few that do not quite fall into the ordinary category. Two analyses of calcite are given below. These are as nearly pure specimens of calcium carbonate as one is likely to find in nature except picked crystals of Iceland

spar. Another is marble, and a curious fact may be recorded of that. If a close analysis is made it will be found that the CaO and CO₂ do not quite balance, the CaO being slightly in excess. As marble has been formed from other varieties of CaCO₃ at a high temperature under pressure, this is natural enough, as some CO₂ must have almost certainly escaped in the process. Another example is coral, of which two examples are given. Siliceous constituents in coral may conceivably be part of the anatomy of the insect, but is much more likely to be fine sand which has been entangled in the growth. Small sea shells and oyster shells dumped from canning factories are also a source of supply of calcium carbonate, and, provided there is not too much difficulty in freeing them from extraneous sand are quite suitable.

	Calcite		Marble	Coral		Shell
Silica	0'10 }	0'20	{ 0'06	0'06	4'53	2'8
Insoluble	0'10 }		{ --			
Ferric Oxide	---	0'12	0'06	0'31	1'95	{ 0'20
Alumina	---		---			{ 0'90
Lime	55'90	55'74	55'66	54'71	51'14	52'40
Magnesia	---	0'13	0'01	0'28	0'52	0'13
Sulphuric Anhydride	---	---	---	---	0'10	0'27
Carbonic Anhydride	43'85	43'66	43'60	42'72	40'40	40'80
Water	0'05	{ 0'10	---	{ 1'38	1'36	{ 2'60
Alkalies and loss		{ 0'05	---	{ 0'54		{ ---
	100'00	100'00	100'02	100'00	100'00	100'04

BLUE LIAS DEPOSITS

I now pass to the consideration of another class of raw materials, *i. e.* blue lias lime deposits. In this country they stretch from the N.E. to the S.W., and have almost a uniform composition. They are intercalated with a calcareous shale which contains so much CaCO₃ as not to differ greatly in its composition from the limestone, but there is a fundamental physical difference. Blue lias limestone is a hard compact stone little affected by water. Its companion the shale, when dry, may appear equally hard and compact, but when exposed to weather goes to mud. The effect is best seen at a place like Lyme Regis, where the coast, consisting of the blue lias formation, is subject to erosion. The cliff falls bit by bit and lies on the foreshore. The shale is slowly

¹ Corresponding to 99'09 % Calcium Carbonate = 55'49 Lime.

washed away, but the limestone is merely rounded like any other shingle. So well was this recognised that small ships used to come to Lyme Regis (and probably do so still) to gather up these stones and convey them to South Wales, where they are burnt to blue lias lime.

Deposits of this kind are particularly well suited for the manufacture of Portland cement, but as the range of composition of the different layers of limestone and shale may be considerable, the strictest chemical control is essential if the manufacture is to be commercially successful.

As indicating the range of composition of the limestone and intercalated shale, the following examples may be cited—

Limestones.				
Silica	12.75	{ 2.03 }		12.64
Insoluble		{ 13.02 }		
Ferric Oxide	2.88	{ 1.00 }		5.42
Alumina		{ 1.04 }		
Lime	45.62	44.84		43.28
Magnesia	0.91	1.15		1.30
Sulphuric Anhydride	0.72	0.16		0.35
Carbonic Anhydride	36.34	33.70		36.56
Water		{ 2.86 }		
Alkalies and loss	0.78	{ 0.20 }		0.45
	100.00	100.00		100.00

Shales.					
Silica	32.55	37.77	52.80	40.34	38.41
Ferric Oxide	2.26	3.41			
Alumina	8.44	5.38	14.26	11.14	12.07
Lime	27.91	27.34	14.76	23.06	23.29
Magnesia	2.27	1.10	1.42	1.42	1.35
Sulphuric Anhydride	Trace	—	—	—	—
Carbonic Anhydride					
Water	22.56	23.32	14.62	22.26	22.01
Alkalies and loss	4.01	1.68	2.14	1.78	2.87
	100.00	100.00	100.00	100.00	100.00

It will be seen that there is ample variation to allow of adjustments from the different strata so that the ultimate mix shall

be of the right composition, but unceasing vigilance is necessary, and the notion that a deposit of this kind can be used as a raw material by merely tearing down the whole face of the quarry, and mixing it is now happily discarded.

MARLS

There are many other materials which are both calcareous and argillaceous and may be termed generically marls. The best known examples are those found in the Cambridgeshire district, where much of the material has a composition nearly appropriate for making Portland cement, but in modern practice is carefully brought to the correct composition and thus makes good cement.

CAMBRIDGE MARLS

Silica	17.20	18.20	18.00	16.70
Alumina	3.06	4.04	4.49	3.60
Oxide of Iron	2.44	2.76	2.91	2.50
Calcium Carbonate	74.60	74.00	73.00	75.30
Magnesia	1.00	0.44	0.94	0.94
Undetermined	1.70	0.56	0.66	0.96
	100.00	100.00	100.00	100.00

CAMBRIDGE MARLS

Silica	17.80	19.80	14.46	16.41
Alumina	3.79	4.05	4.11	3.13
Oxide of Iron	2.41	2.75	2.89	2.08
Calcium Carbonate	74.60	72.60	77.10	76.20
Magnesia	0.72	0.47	0.80	0.94
Undetermined	0.68	0.33	0.64	1.24
	100.00	100.00	100.00	100.00

It will be seen that these range from a material which, when burnt, will give a cement, *per se*, to those which are of value only as additions to more calcareous materials. This useful property has led to many mistakes. The deposits in Cambridgeshire and similar deposits in Belgium have been burnt without any attempt to regulate their composition, and although they have produced cement of fair quality, they could not in the nature of things provide a true Portland cement. This has led to a bad reputation for cement made in both places—a reputation most unjust to the genuine Portland cement, which is

produced at both places. Sold under its proper name, cement made by the direct burning of a suitable marl is a legitimate product, but sold as Portland cement it is a fraud. In this connection it is pertinent to quote a case which is within the author's personal knowledge. Cambridgeshire cement, made from a marl of the sort quoted above, was being sold as "blue lias lime"; there is no blue lias formation in Cambridgeshire, and the firms who produced genuine blue lias lime brought an action against those purveying the Cambridgeshire material. The equity was clear enough, but the blue lias people lost their case on the ground that a trade custom had grown up of calling hydraulic lime "blue lias lime," irrespective of its origin. As *obiter dicta* it may be said (a) that a custom of the kind should be keenly watched by the trade affected and stopped before it becomes recognised in law; and (b) that action should be taken in the High Court instead of before a stipendiary (as is usually done), as the Court is then more competent to decide highly technical points. The instance given is by no means a solitary one; within the author's experience similar incidents have happened sometimes in quite different materials, much to the disadvantage of the honest trader.

The next material to be considered is clay and its congeners.

CLAYS

The typical argillaceous material used in cement manufacture is some form of clay, and examples of the chemical composition of such clays are given below.

	Medway Clay.			Gault Clay.	
Silica	58.73	55.29	58.08	33.28	55.15
Alumina	18.29	16.38	14.55	13.57	12.26
Ferric Oxide	7.84	7.35	9.89	6.37	4.36
Lime	0.62	—	0.75	17.92	10.14
Magnesia	2.24	0.21	1.99	1.54	1.89
Sulphuric Anhydride	—	3.21	—	0.71	Trace
Carbonic Anhydride	12.28	17.56	14.74	15.38	15.47
Water	—	—	—	7.98	—
Alkalies and loss	—	—	—	3.25	0.73
	100.00	100.00	100.00	100.00	100.00

	N. England.	N. Ireland.	S. Wales.	
Silica	47'18	46'00	64'38	56'96
Ferric Oxide	7'30	5'00	22'40	18'16
Alumina	25'66	14'26		
Lime	1'52	7'16	1'14	7'80
Magnesia	1'80	4'06	2'40	1'81
Sulphuric Anhydride	Trace	0'31	—	—
Carbonic Anhydride	13'10	{ 6'18 }	6'08	10'16
Water		{ 8'57 }		
Alkalies and loss	3'44	8'46	3'60	5'11
	100'00	100'00	100'00	100'00

	Jamaica.	Hong Kong.	
Silica	58'18	53'26	53'62
Ferric Oxide	7'92	1'90	2'14
Alumina	20'36	30'10	29'58
Lime	2'56	0'32	0'12
Magnesia	1'66	0'63	0'99
Sulphuric Anhydride	0'16	Trace	Trace
Carbonic Anhydride	8'14	12'44	11'30
Water			
Alkalies and loss	1'02	1'35	2'25
	100'00	100'00	100'00

	S. America.			
Silica	55'64	55'26	48'36	59'46
Ferric Oxide	3'82	4'77	6'20	6'55
Alumina	21'36	23'09	15'56	18'01
Lime	0'32	0'82	0'00	0'34
Magnesia	1'72	1'18	3'82	1'01
Sulphuric Anhydride	0'41	0'99	2'23	0'65
Carbonic Anhydride	11'96	9'80	11'70	8'40
Water				
Alkalies and loss	4'77	4'09	6'13	5'58
	100'00	100'00	100'00	100'00

CEMENT

	Siam.		
Silica	68'14	77'92	76'66
Ferric Oxide	3'52	4'10	5'16
Alumina	7'22	8'50	8'68
Lime	9'04	0'96	0'24
Magnesia	0'46	0'38	0'50
Sulphuric Anhydride	Trace	Trace	Trace
Carbonic Anhydride	6'47 }	6'12	6'50
Water	4'23 }		
Alkalies and loss	0'92	2'02	2'26
	100'00	100'00	100'00

	Mexico.		Russia.		
Silica	61'96	49'10	51'50	52'70	53'96
Ferric Oxide	5'10	4'62	6'65	6'80	7'77
Alumina	13'84	11'84	22'19	21'70	22'73
Lime	4'12	10'00	2'22	2'04	0'84
Magnesia	1'37	2'52	1'37	1'44	1'17
Sulphuric Anhydride	0'09	4'22	Trace	Trace	Trace
Carbonic Anhydride	9'60				
Water		17'70	12'40	12'04	8'48
Alkalies and loss	3'92		3'67	3'28	5'05
	100'00	100'00	100'00	100'00	100'00

	Sweden.	
Silica	34'28	52'08
Ferric Oxide	4'41	7'00
Alumina	9'25	12'26
Lime	24'16	8'80
Magnesia	2'46	2'45
Sulphuric Anhydride	Trace	Trace
Carbonic Anhydride	19'30	6'61
Water	3'68	5'85
Alkalies and loss	2'46	4'95
	100'00	100'00

	Singapore.		
Silica	53.90	51.22	47.80
Ferric Oxide	4.91	3.57	7.00
Iron Pyrites	2.19	2.63	—
Alumina	18.19	16.18	18.82
Lime	3.18	0.42	0.76
Magnesia	1.60	0.89	1.25
Sulphuric Anhydride	0.29	1.63	1.11
Carbonic Anhydride			
Water	15.74	23.46	23.26
Alkalies and loss			
	100.00	100.00	100.00

	India.			
Silica	37.66	58.02	60.76	58.04
Ferric Oxide	5.71	7.56	7.98	8.68
Alumina	9.86	15.50	14.52	13.34
Lime	21.78	2.84	2.26	6.02
Magnesia	2.00	1.95	2.08	2.52
Sulphuric Anhydride	Trace	Trace	Trace	Trace
Carbonic Anhydride				
Water	21.00	7.70	7.04	9.50
Alkalies and loss	1.96	6.43	5.36	1.90
	100.00	100.00	100.00	100.00

	W. Indies.	
Silica	54.35	56.99
Ferric Oxide	10.03	10.18
Alumina	22.42	17.83
Lime	2.99	2.14
Magnesia	1.60	1.29
Sulphuric Anhydride	Trace	Trace
Carbonic Anhydride		
Water	8.61	11.57
Alkalies and loss		
	100.00	100.00

It will be seen from these analyses that there is a large range of composition within which clays are suitable for making

cement. As previously observed, the local conditions must be regarded and the clay must be chosen in relation to the calcareous material with which it will be used. The plain straightforward case of a typical clay and a typical limestone or chalk rarely occurs, and any attempt to lay down a general rule would be misleading. The calculation of the composition obtainable from any two materials involves nothing but ordinary arithmetic, but decision as to whether a deposit of both substances is of commercial value is a much more complicated matter, depending as it does on such factors as the cost of transport and fuel.

SHALES

A selection of analyses of shales is given: like the clays, their composition varies, and must always be regarded in relation to the calcareous material with which they are to be used.

	N. Wales.	Ireland.
Silica	60.54	44.53
Ferric Oxide	8.05	2.28
Alumina	19.59	8.34
Lime	0.34	20.12
Magnesia	1.50	0.82
Sulphuric Anhydride	Trace	—
Carbonic Anhydride	—	20.30
Water	4.78	3.61
Alkalies and loss	5.20	—
	100.00	100.00

	S. Russia.	Egypt.	
Silica	57.60	23.58	31.59
Ferric Oxide	10.47	4.36	5.19
Alumina	16.77	12.45	17.44
Lime	1.42	27.20	18.18
Magnesia	2.05	1.28	1.50
Sulphuric Anhydride	0.07	0.48	0.20
Carbonic Anhydride	8.68	20.92	13.57
Water	—	9.12	11.43
Alkalies and loss	2.94	0.61	0.90
	100.00	100.00	100.00

	India.				
Silica	46.98	43.52	43.16	41.70	54.84
Ferric Oxide	12.65	12.08	12.18	9.32	10.50
Iron Pyrites	2.55	0.36	3.36	4.39	—
Alumina	19.59	21.40	22.38	20.69	18.00
Lime	1.34	3.34	1.96	1.94	1.68
Magnesia	1.41	2.30	2.33	2.34	2.53
Sulphuric Anhydride .	Trace	Trace	Trace	Trace	Trace
Carbonic Anhydride .		12.84			8.52
Water	15.48		14.63	19.62	
Alkalies and loss . .		4.16			3.93
	100.00	100.00	100.00	100.00	100.00

	Rhodesia.	E. Africa.	
Silica	55.64	56.20	58.18
Ferric Oxide	1.10	8.91	8.57
Alumina	20.32	17.69	14.83
Lime	2.40	0.96	3.34
Magnesia	0.38	2.95	2.52
Sulphuric Anhydride .	Trace	Trace	Trace
Carbonic Anhydride .			
Water	10.52	13.29	12.56
Alkalies and loss . .	3.64		
	100.00	100.00	100.00

NATURAL CEMENT ROCKS

There are various substances of less importance than those given above which ought certainly to be included as valuable raw materials for the production of hydraulic cement. These are as follows—

NATURAL CEMENT ROCKS (*American*), (ECKEL)

	Rosen- dale, N.Y.	Louis- ville, Ind.	Lehigh, Pa.	Hancock, Mary- land.	Utica, Ill.	Buffalo, N.Y.
Silica	15.37	13.65	18.34	19.81	12.22	9.03
Ferric Oxide	2.25	1.45		2.41	3.90	0.85
Alumina	9.13	3.46	7.49	7.35	9.39	2.25
Lime	25.50	34.55	37.60	35.76	24.40	26.84
Magnesia	12.35	7.97	1.38	2.18	10.43	18.37
Carbonic Anhydride .	34.20	35.92	31.06			40.33
Water	1.20		13.94	31.74	38.48	0.98
Alkalies and loss . .	—	3.00	0.19	0.75	1.18	1.35
	100.00	100.00	100.00	100.00	100.00	100.00

These analyses, which are given by Eckel in his well-known book, indicate the considerable range of composition of cement rocks used in the United States. Perhaps the best known and most characteristic is the material from Rosendale in the State of New York. Its most noteworthy constituent is magnesia, which in Portland cement is looked upon with considerable suspicion, if in more than a small quantity. But natural cement rocks are burnt at a comparatively low temperature, and the magnesia not only causes no ill effect but may itself act as a cement. Whether this is so or not, the value of natural cement of this class has been repeatedly proved in practice on a large scale, as although its strength is low it is sufficient for many purposes and can be easily and cheaply manufactured. Three others in the list of analyses are similar to Rosendale cement rock in that they contained a considerable percentage of magnesia, but the other two—Lehigh and Hancock—more nearly resemble natural cement raw materials, such as the various hydraulic limes and Roman cements, their percentage of magnesia being similar to that in Portland cement, although their composition as a whole differs therefrom materially.

BELGIAN NATURAL CEMENT ROCK

Silica	15.75
Alumina	3.95
Ferric Oxide	1.00
Lime	43.10
Magnesia	6.49
Sulphuric Anhydride	0.50
Carbonic Anhydride	35.21
Water	
	100.00

In the case of the example quoted above, the composition approaches so nearly to that of the raw material as artificially mixed for making Portland cement that the Belgian "natural cement" has sometimes been sold for Portland cement. The procedure is not legitimate and has probably died out. There are deposits in this country and in other parts of the world whose composition is so similar to that of an artificial mixture of raw materials for Portland cement that many attempts have been made to use the deposits as they occur, without adjust-

ment of composition. These attempts have failed uniformly, for although a cement of moderate quality can be made, yet it is not Portland cement, and will not pass the tests of the British Standard Specification.

When, however, the raw materials are corrected in composition by the addition of a little chalk or clay, and mixed intimately so as to provide a raw material varying in composition within the usual narrow range, they make Portland cement of excellent quality, and works of considerable size are using them in this way.

ROMAN CEMENT STONE

An excellent instance of what is really a sort of cross between hydraulic limestone and Portland cement is afforded by the cement made by burning the nodules used for making Roman cement. As stated in the earlier part of the book, the nodules are dredged and burnt just as they come to hand, and on account of their relatively high content of alumina and ferric oxide are burnt easily at a low temperature. The nodules are characterised by their containing both manganese and ferric oxide, to which the colour both of the nodules and of the cement is due. The following are three analyses of this raw material—

	Sheppey.		Harwich.
Silica	16.90	17.20	21.90
Alumina	6.73	6.80	3.50
		} including	} including
Ferric Oxide	5.11	12.80	8.20
		MnO ₂	MnO ₂
Manganese Oxide	0.92	—	—
Lime	34.02	29.34	32.37
Magnesia	2.19	3.33	2.71
Sulphuric Anhydride	0.21	—	—
Carbonic Anhydride	28.62	26.73	28.42
Soda (Na ₂ O)	0.88	—	—
Combined water, organic matter and loss }	3.82	3.80	2.90
	100.00	100.00	100.00

In two of the analyses the percentage of manganese is not separately stated, but it is a characteristic constituent. This raw material by itself is unfitted for making Portland cement, but might be used in admixture with more calcareous material. As the industry is purely local and the output small, this is not

likely to occur, and, although Roman cement is an excellent material, its use is limited, and is not likely to extend.

HYDRAULIC LIMESTONES

	Teil, Gaillart quarry.	France, Lafarge quarry.	France, Plassac.	Alsace, Metz.
Silica	13.75	14.30	11.20	11.03
Alumina	0.65	0.70	5.30	3.75
Ferric Oxide	Trace	0.80	4.00	5.07
Lime	47.00	46.50	35.50	43.02
Magnesia	—	—	5.85	1.34
Carbonic Anhydride	36.93	36.54	34.35	35.27
Water, Alkalies and loss	1.67	1.16	3.20	0.52
	100.00	100.00	100.00	100.00

GRAPPIERS

	Teil.	Senonches.
Silica	26.0	25.5
Alumina	3.5	3.6
Ferric Oxide	0.8	0.7
Lime	66.0	68.0
Magnesia and Sulphur Dioxide	1.0	1.3
Water, Carbonic Anhydride and Alkalies	2.7	0.9
	100.0	100.0

It is convenient to incorporate these analyses here. They may be best read in connection with those of the finished cement.

The analyses of several types are given; those from the Teil district are remarkable for their high content of silica and the small percentage of alumina and ferric oxide. Such a siliceous limestone would be of little value for making hydraulic lime, were it not for the fact that the silica is in so fine a state of division that it unites easily with the lime, in spite of the absence of ferric oxide and alumina, which in ordinary Portland cement serve as fluxing agents. The other two examples are of a different class. Both contain an ample amount of alumina and ferric oxide, and yield hydraulic limes relatively quick setting and resembling Roman cement. In the case of the Teil limes,

setting is slow, and if there is a surplus of lime over and above that combined with the silica, slaking is necessary and is practised on a large scale, so much water being used as will hydrate this surplus lime, and leave the cementitious silicate untouched. In the course of this slaking it is found that parts of the burnt lime have conglomerated into clinkered masses (called "grappiers," *v. s.*), and these are easily removed by sifting. They are the product of the action of the lime on any portions of the limestone which are not solely siliceous but contain also some alumina and ferric oxide, and, in fact, are Portland cement clinker. When ground they make excellent Portland cement. It must be understood that this material is merely a by-product of the great industry of hydraulic lime, practically free from alumina and ferric oxide.

Other hydraulic cement materials may be mentioned, and analyses are given.

BLAST FURNACE SLAGS

Silica	29'70	29'60	31'60	32'30	33'20	35'00
Alumina	16'33	13'78	15'27	16'26	14'91	14'43
Ferrous Oxide	0'51	1'03	0'52	0'13	0'51	0'51
Manganous Oxide	2'98	2'98	2'23	1'49	4'16	4'64
Lime	42'16	45'02	41'82	40'66	39'93	38'80
Magnesia	3'59	3'60	3'80	3'38	3'54	2'88
Phosphoric Anhydride	0'14	0'10	0'11	0'11	0'10	0'16
Calcium Sulphide	4'68	3'83	4'36	5'51	3'69	3'47
	100'09	99'94	99'80	99'84	100'04	99'89
Total CaO	45'80	48'00	45'20	45'20	42'80	41'50
Total Mn	2'31	2'31	1'73	1'15	2'90	3'60
Total S	2'08	1'70	1'94	2'27	1'64	1'54

The type of slag best fitted for the manufacture of Portland cement is one which is as basic as possible. The term must not be confused with "basic slag," which has nothing to do with the blast furnace, and merely means the slag obtained as a useful manurial by-product from the basic process of making steel from phosphoric ores. In the case of blast furnace slags suitable for making Portland cement the word "basic" is used in its accurate sense. Such slags contain a large quantity of lime, and consequently the ratio of basic to acid oxides is correspondingly high. Frequently the ratio of alumina to silica is somewhat high, and the resulting cement, if prepared from such

slag with a suitable addition of nearly pure limestone, will be too aluminous, and therefore too quick-setting. But if the limestone itself is siliceous it may be practicable to correct the ratio of silica to alumina and manufacture a Portland cement normal in that respect. In this, as in many other instances which have been cited, each case must be judged on its merits. There is no golden rule; it is the result which must be held steadily in view.

There is another material which can be used for the production of Portland cement. The analyses are set out below.

ALKALI WASTE (*Ammonia Process*)

Silica	1'90	0'60
Alumina	1'41	
Ferric Oxide	1'38	3'04
Lime	48'29	53'33
Magnesia	1'51	0'48
Sulphuric Anhydride	1'26	—
Carbonic Anhydride	39'60	42'43
Alkalies	0'64	0'20
Water	3'80	—
	99'79	100'08

Two samples are given of waste made by the ammonia-soda process, which, as may be expected from the nature of the process, is practically pure calcium carbonate. Obviously, material of this kind is suitable for making Portland cement if mixed with clay of appropriate composition.

Alkali waste from the Leblanc process, which has been treated by the Chance process for the recovery of its sulphur and has thereby been converted into carbonate of lime, is also used. It contains varying amounts of sulphur not eliminated by the Chance process, and in consequence may be less easy to deal with than waste from the ammonia-soda process, because the quantity of sulphur permissible in the finished cement is limited by all standard specifications. The reason for this is dealt with in the section on cement itself.

PUZZOLANAS, TRASS, ETC.

Quite a different sort of cement raw material is represented by the puzzolanas. They could doubtless be used for making

Portland cement by appropriate admixture with limestone of suitable composition and then burning at a proper temperature, but they are too useful in another capacity to be employed in this way. They, without burning, will, when mixed with lime, form excellent hydraulic cements, part of their silica being active enough to combine directly with the lime in the presence of water. It is difficult to discriminate between the silica which is active and that which is a mere diluent such as is sand, and even the best analyses depend on arbitrary conditions. Normally the active silica is regarded as that which can be extracted from the material by a weak alkali, such as 1 % caustic soda solution, but there is no fixed method. Naturally much depends on the state of subdivision of the material. If very finely ground, a considerable amount of silica otherwise inert will come into play. Such a matter is a commonplace of physical chemistry, but its bearing on the present question has scarcely been recognised among those using puzzolanas. In fact, these are often used in their double capacity—

- (1) As a substitute containing silica active enough to combine directly, and in the cold, with lime.
- (2) As an aggregate.

The latter function means the waste of so much good cementitious material, but if there is no other suitable aggregate on the spot it is intelligible and justifiable.

PUZZOLANA

	Roman.	Neapolitan.
Silica	32·64	27·80
Insoluble	25·94	35·38
Alumina	22·74	19·80
Ferric Oxide		
Lime	4·06	5·68
Magnesia	1·37	0·35
Sulphuric Anhydride	Trace	Trace
Carbonic Anhydride	8·92	4·27
Water		
Alkalies	4·33	6·72
	100·00	100·00

TRASS

	Java.	Nevis.	St. Kitts.
Silica	50'40	68'97	57'85
Insoluble	19'32	—	—
Alumina	13'86	14'83	17'71
Ferric Oxide	3'10	7'69	9'24
Lime	Nil	2'52	5'84
Magnesia	0'13	0'27	0'74
Sulphuric Anhydride	—	—	—
Carbonic Anhydride	—	—	—
Water	12'61	1'59	5'06
Alkalies	0'32	4'13	3'56
	99'74	100'00	100'00

The raw materials being of satisfactory quality, the next point is their handling. There are three things to be considered: the calcareous material, the argillaceous material, and the fuel. It is impossible to generalise on this question. Every proposition must be considered on its merits, and unless an intimate knowledge is available concerning the cost of quarrying and of freights, the most promising undertaking may not succeed. Generally speaking, however, as the quantity of fuel is roughly 50% of the cement made, for burning and for power, its cost, within reason, counts little unless the place is remote, but it may be a serious and even prohibitive item when it has to be conveyed a long way. There are many fine deposits now undeveloped entirely from this difficulty of obtaining fuel on the spot at a reasonable price. The question of fuel is dealt with in a separate section.

It is important, also, to ascertain the physical character of the raw materials. This is often overlooked when a cement undertaking is being considered. Although the ultimate analysis of the calcareous or argillaceous material may seem to be in every way suitable, it does not follow that cement can be made economically from these substances. Suppose, for instance, that the clay is not a true clay but a silt in which there is a large quantity of sand, sometimes fairly coarse, naturally this must be ground to a fineness which will allow it to mix so closely with the calcareous particles that complete union must ensue. The same statement holds good with the limestone or chalk, though the case is rarer. In any event, a chemical analysis alone is not sufficient; a mechanical analysis is useful, and both must be controlled by the knowledge of the class of materials which can only be gained by experience.

CHAPTER III

FUEL

RAW materials, however abundant in quantity and excellent in quality, are useless for the manufacture of cement unless there is an adequate supply of fuel at a reasonable cost. It is this factor which has hindered so many promising enterprises; when too much attention was directed to the raw materials, and the fuel question was not fully considered. It is true enough that the total quantity of fuel for burning the raw materials and for the production of power is, in round figures, only some 50 % of the weight of cement produced, and, speaking generally, there is little difficulty in obtaining a sufficiency of fuel at the spot where the manufacture is to be carried on. It happens, however, in some cases that local fuel is so poor in quality and the cost of carriage of better fuel is so high that an undertaking, sound in all other respects, is either prevented altogether, or has but a fluctuating and precarious existence.

In the earlier days of cement manufacture, before the introduction of the rotatory kiln, the principal fuel used was coke. In the earliest type of kiln, which is described under its proper heading, coke was mixed with the mixed raw materials, which were in the form of irregular lumps, just as they came from the drying-floors, precisely as it is mixed with lumps of limestone or chalk in making ordinary lime. In these older works the coke was prepared in a somewhat primitive coke oven, and the waste heat was used for drying the raw materials, which were pumped out on to the floors in the form of slurry.

Oven coke, as prepared for blast furnaces and for foundry use, is particularly hard and dense, so as to carry the burden of these furnaces, and at the date when coke was used in making cement it was generally prepared in beehive ovens from which the by-products—tar, gas, and ammonia—were not recovered. Nowadays recovery ovens are almost universal when coke is made for metallurgical purposes. But in the early days of cement industry recovery ovens were in their infancy, and the cement

maker used a non-recovery oven of the type then common. As he did not need to obtain a particularly hard and dense coke, he modified the oven to some extent, and did not push the coking so far as is necessary for smelting, but he was still confronted with the fact that his by-products went to waste. Thus it came about that it was considerably cheaper to buy gas coke than to make the coke at the cement works.

ANALYSES OF COKE

OVEN COKE

	British.		French.		American.	
Carbon	83.40	91.88	89.27	91.04	87.47	90.37
Ash	3.50	6.91	7.80	5.90	11.32	7.95
Sulphur	0.81	1.21	N.D.	N.D.	0.69	0.90
Water	0.99	—	0.59	0.23	0.49	0.78
Calorific Value . .	7811	8020	7920	8036	8070	7983

GAS COKE

Carbon	88.99	88.86
Ash	9.62	6.41
Sulphur	1.39	0.96
Water	—	3.73
Calorific Value . .	7865	7938

It will be seen that the chief chemical difference in the cokes, whether oven or gas cokes, depends on their content of ash, water and sulphur. The ash is important, as it will materially affect the composition of the cement which is burnt in contact with it. The same remark applies to the sulphur, which, by forming sulphates during combustion, will considerably modify the setting-time of the cement. This subject is dealt with in the section on cement. The water and ash are, of course, diluents, and decrease the calorific value of the fuel. The fuel value, as distinct from the influence of these diluents, is best ascertained by the direct determination of the calorific value.

Coke breeze, which is the small refuse of gas coke, has also been used, generally by mixing it with the slurry, so as to provide fuel in the heart of the raw material being burnt. It is a serviceable material, but has the drawback of containing usually a considerable percentage of ash and sulphur, both of

which influence the quality of the cement. Analyses of three samples of coke breeze are here given.

COKE BREEZE

Moisture	15·82	12·88	4·50
Carbon	52·00	75·08	61·34
Ash	32·18	12·04	34·16

The foregoing analyses show the general composition of the breeze. It is a comparatively poor fuel, containing as it does a good deal of both water and ash, diluents both. It has been used in fixed kilns, both interspersed between the lumps of raw material, and mixed with the raw material before this is fed into the kiln. The high percentage of ash, in either case, forms afterwards an integral part of the cement, as although correction for its influence on the composition as a whole may be made, yet it is impossible to eliminate its local effect. Where an ashy piece of breeze is in contact with a mass of cement raw material there is an excess of siliceous matter, and the product at that point no longer has the normal composition of Portland cement, however carefully the original proportions of calcareous and argillaceous materials have been adjusted. It follows that in modern manufacture, where close and accurate work is the rule, the use of a variable material capable of deranging the normal composition of the product is discountenanced.

At the present time small coal is generally used for firing rotatory kilns, which alone need be considered in this respect. Such small coal as has been used for firing fixed kilns is of a similar class, and needs no separate description.

COALS FOR BURNING CEMENT

	South Wales.		Derbyshire.	Lancashire.
Moisture	1·73	—	—	—
Volatile Hydrocarbons	30·17	27·00	41·00	42·00
Fixed Carbon	64·58	69·08	56·30	53·12
Ash	3·52	4·91	2·65	4·88
Sulphur	—	1·43	1·01	1·44
Caloric Value	8078	8402	8120	8113

CEMENT

	Newcastle.	Ryhope.	Silksworth.	Average Midland.
Volatile Hydrocarbons	39'00	28'77	26'51	29'56
Fixed Carbon	57'23	59'92	63'95	57'73
Ash	3'77	11'31	9'54	12'71
Sulphur	1'24	—	—	—
Calorific Value	8446	—	7639	7117

Other examples of similar coal are given below—

Moisture	6'79	8'66	9'59	6'27
Volatile Hydrocarbons	37'07	37'42	35'56	36'98
Fixed Carbon	47'96	47'13	46'45	51'27
Ash	8'18	6'79	8'40	5'48
Sulphur	1'50	0'65	0'97	1'98
Calorific Value	6737	6514	6302	6830

Moisture	10'99	7'74	3'19	7'29
Volatile Hydrocarbons	31'88	31'92	31'76	32'80
Fixed Carbon	52'90	55'51	58'40	55'41
Ash	4'23	4'83	6'65	4'50
Sulphur	1'99	1'98	2'23	1'00
Calorific Value	6973	7335	7573	7438

INDIAN

Moisture	7'13	5'42	7'73	8'22
Volatile Hydrocarbons	38'01	37'53	34'82	36'84
Fixed Carbon	36'10	33'32	33'90	34'82
Ash	18'76	23'73	23'55	20'12
Sulphur	3'89	6'14	2'98	3'75
Calorific Value	5270	5182	4825	5288

AMERICAN

Moisture	2'08	1'40	1'00	4'90	0'90
Volatile Hydrocarbons	35'41	39'52	39'37	38'00	30'42
Fixed Carbon	56'15	51'69	55'82	51'72	60'30
Ash	6'36	6'13	3'81	5'38	8'38
Sulphur	1'30	1'46	0'42	—	—

RUSSIAN

Moisture	1'30	1'10	1'20	2'70
Volatile Hydrocarbons	29'20	26'00	29'50	30'70
Fixed Carbon	57'90	59'00	58'10	48'00
Ash	11'60	13'90	11'20	18'60
Sulphur	1'30	1'10	1'10	1'50
Calorific Value	7140	7015	7150	6280

These coals represent the usual range of fuel of this class suitable for burning cement in rotatory kilns. It will be seen that although they vary, as their proximate analyses show, yet, generally speaking, they are of the same type, *i. e.* they are coals with a fairly large amount of volatile bituminous matter, whilst the ash is usually not more than 10 % or 12 %. As the ash increases the practical difficulties in burning also increase, quite apart from the question of the lower calorific value. But it is possible under special circumstances to use even a very poor and ashy coal, as shown by the following analysis of a coal from the Argentine.

ARGENTINE COAL

Moisture	6'34
Volatile Hydrocarbons	20'64
Fixed Carbon	28'28
Ash	44'74
Sulphur	0'55

This seems a most unpromising material, but nevertheless it was successfully burned in a rotatory kiln on a manufacturing scale, and produced excellent cement.

Lignite can also be used. The following analysis may be cited—

Moisture	25'92
Volatile Hydrocarbons	47'83
Fixed Carbon	23'33
Ash	2'92

The ash is a little lower than usual, but in other respects the analysis is typical. It is almost needless to say that great skill and care are necessary in handling inferior fuels of this kind.

It may be said that at the present time by far the most important fuel for cement making is small coal, but there are other fuels which have been proposed and used.

Producer gas has been used for burning lime, but not, as far as I know, for burning cement in fixed kilns. It has been repeatedly and thoroughly tried in rotatory kilns. In fact, what is probably the earliest form of rotatory kiln, devised by Ransome some forty years ago, was fed with producer gas, and the Stokes kiln, about ten years later, was similarly fired. In both cases the method was unsuccessful, the chief reason being that it is not easy to maintain a high uniform temperature with producer gas as a fuel, unless there is appended some system of regeneration. This is simple enough with glass or steel furnaces, but not easy with a cement furnace, when the quantity of dust carried by the burning gas would seriously impede the action of the regenerating chambers. No doubt it is perfectly possible to use producer gas, but the problem was solved by the use of powdered coal, and there is no such advantage in the employment of producer gas as to induce inventors and manufacturers to pursue the quest.

If it were practicable to use a fuel gas of higher calorific value than producer gas—*e. g.* coal gas or natural gas—cement burning could be conducted under ideal conditions, but in the case of coal gas the cost is prohibitive, and a natural gas is a rare commodity now, and in places where it still occurs cannot be reckoned as a constant source of fuel.

Oil firing has, however, been used with complete success, and is an admirable method when oil can in any way compete with coal in price. The simplest possible apparatus is necessary, merely a sort of blowpipe such as is used in flare lamps made on a large scale, the oil being injected by air or steam. But except in very special cases oil fuel is too dear to compete with powdered coal. Examples of fuel oil suitable for furnace work are given below. It will be seen that the percentage of sulphur varies and in some cases is rather high, but this is not of great importance, and decision as to whether a given oil can be used depends on its calorific value and its cost compared with that of the coal on the site of the works.

FUEL

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FUEL OILS

Carbon	86.82	84.66	84.57	89.20
Hydrogen	12.34	11.98	11.75	6.93
Sulphur	0.59	2.97	2.80	1.05
Nitrogen	Trace	Trace	Trace	Trace
Calorific Value	10,646	10,514	10,435	9,181

Carbon	83.40	85.87	85.56
Hydrogen	11.29	11.35	11.69
Sulphur	4.00	1.10	1.01
Nitrogen	0.37	—	—
Calorific Value	10,181	10,344	10,418

There is another mode of burning cement which may yet be put into practice. It is electrical heating. Naturally, it would only be put into use in those places where coal is very dear, *houille blanche* very cheap, and raw materials abundant and good. It may be of interest to make a comparison between the two methods of heating. It may fairly be assumed that the average quantity of coal needed is about 25 % of the weight of the cement made, taking the coal as having a calorific value of 7500 calories.

To burn 1000 kilos of cement would therefore need 250 kilos of coal of this calorific value. This amount of heat corresponds with 2165 Board of Trade Units (kilo watt hours). Assuming that the heat losses are equal in the two systems, a tabular comparison of the cost of each may be made.

COST OF BURNING 1000 KILOS OF CEMENT

With 25 % of coal of 7500 calories at 16s. per 1000 kilos	= 4s.
With electrical energy at $\frac{1}{4}$ d. per Board of Trade Unit	= 45s.
" " " " $\frac{1}{16}$ d.	= 18s.
" " " " $\frac{1}{16}$ d. (= £2 per kilo watt year)	= 10s.

Two pounds per kilo watt year may be taken at as low a figure as is likely to be attained, and it is clear that even with this low cost burning electrically is much dearer than burning with coal in the ordinary way. It should be noted, however, that this comparison rests on the assumption that all the losses of heat are identical in both cases.

This, however, will not be the case, because although the number of calories necessary to decompose the calcium carbonate will be the same whatever method of heating is used, yet the

heat carried away by the gases will differ. When coal is used the products of combustion must be heated as well as the carbonic anhydride from the calcium carbonate, whereas in electrical heating only the latter comes into account. It is convenient to consider the dry process first. To produce 1000 kilos of cement 1125 kilos of calcium carbonate must be decomposed, and they will yield 495 kilos of carbonic anhydride, which, at a temperature 300° C. above that of the atmosphere, represents 35,640 calories. The products of combustion of 250 kilos of coal weigh approximately 5750 kilos, and for heating this to a temperature of 300° C. above that of the air 414,000 calories are necessary. The decomposition of the calcium carbonate requires 478,012 calories. Therefore we have the consumption of heat for these three purposes thus—

FOR THE PRODUCTION OF 1000 KILOS OF PORTLAND CEMENT

	<i>Calories.</i>
Decomposition of 1125 kilos of calcium carbonate	478,012
Heating carbonic anhydride from calcium carbonate 300° C. above temperature of air	35,640
Heating products of combustion of coal 300° C. above temperature of air	414,000
	<hr/> 927,652 cals.

So that stated in percentages the figures are—

	<i>Calories used.</i>
Decomposition of calcium carbonate	51.5
Heating carbonic anhydride from calcium carbonate	3.9
Heating products of combustion of coal	44.6
	<hr/> 100.0

From this it appears that nearly half the total calories required for burning cement are used for heating the products of combustion of the coal itself, and, taking this fact into consideration, the outlook for electrical heating is more favourable. It must be remembered that in each case a part of the heat is lost by radiation and conduction. No exact computation has been made, but it may be taken at 10 % of the total heat. With this assumption, the table given above will become—

	<i>Calories used.</i>
Decomposition of calcium carbonate	46.4
Heating carbonic anhydride from calcium carbonate	3.5
Heating products of combustion of coal	40.1
Loss by radiation, etc.	10.0
	<hr/> 100.0

On these data the comparison of the cost of burning by coal and electrical energy may be revised.

COST OF BURNING 1000 KILOS OF CEMENT

With 25 % of coal of 7500 calories at 16s. per 1000 kilos	= 4s.
With electrical energy at $\frac{1}{4}$ d. per Board of Trade Unit	= 27s.
" " " " $\frac{1}{10}$ d.	= 10s. 10d.
" " " " $\frac{1}{8}$ d. (= £2 per kilo watt year)	= 6s.

Under the most favourable conditions electrical energy at its cheapest cannot compete with coal at 16s. a ton. But in remote districts coal may cost £4 a ton, and consequently the cost of burning will rise to 20s. per ton of cement produced. It is just that sort of district where abundant and cheap water power may be found, in which case the comparison of cost of burning may well be in favour of the electrical method. In short, each case must be considered on its merits, and it would be rash to conclude that because even when electrical energy is at its cheapest it can only compete with relatively dear coal, there is no possibility of its utilisation when so low a priced commodity as cement is concerned.

The foregoing section on fuel is designed to show how sources of heat very different in themselves can be used for burning cement raw materials, ranging from an intangible form of heat to anthracite. If the question were purely scientific and had no sordid considerations to affect it, there is no doubt as to the best method of burning. It is by electrical heating, as then the ultimate product would be as perfect as the nature of the raw materials allowed, inasmuch as they would be uncontaminated by ash and the temperature could be regulated to a nicety. Unfortunately, as has been shown above, the cost of electrical burning is prohibitive, save in very exceptional circumstances.

The next best method is certainly heating by gas, for very much the same reasons. There is no contamination by ash and regulation of temperature is easy. Where "natural gas," which is substantially methane (CH_4), is available it could be used with the utmost success, but both that and other combustible gases, such as ordinary coal gas, are too costly. The standard industrial gaseous fuel, producer gas, will not by itself give a temperature high enough to form proper clinker, and could only be used with the aid of regenerators. Owing to the fact that in burning cement some dust is likely to be produced

which would prove most objectionable in the regenerators, the cost of these and of the much enlarged burning-chamber would be a heavy burden if the present system of rotatory kilns is to be retained. It is not to be assumed that the rotatory kiln is the last word in cement manufacture, but it is the best at present in use. If the principle is to be retained the size of the kilns must be greatly increased, and the cost of the whole of the burning plant, including the regenerators, would be much larger than the present comparatively simple apparatus. It is to be regretted that at present there is no prospect of the practical use of producer gas for burning cement.

An almost ideal fuel for burning cement is oil, and, as has been said above, can be and has been used with great success. Again cost stands in the way, and at the present time, when the demand for oil of all kinds for many other purposes exceeds the supply, there is no likelihood of oil being used for cement burning.

It comes down, then, to solid fuel. As all fixed kilns of the older type may be regarded as obsolescent, it is not necessary to say more about coke and breeze except to recall that they must be bought on their calorific value, and their water, ash and sulphur, and that the chemical composition of the ash must be taken into account, as it will influence the composition of the cement materially, the more so as each particle of the ash remains on the outside of the piece of clinker with which it is in contact, penetrating but little into the mass. The total *average* composition of the finished *cement* may be correct, but the clinker itself may be considerably over-limed. This question will be more fully discussed in a later chapter.

Coal, then, is now the only fuel of practical importance. As its cost is one of the large items in the manufacture of cement, it behoves the manufacturer to watch his supplies strictly. At the best-managed works this is done as a matter of routine, and prices should be fixed with the same precision as is customary when parcels of ore are dealt in. The chief items naturally are the moisture, volatile matter, fixed carbon, sulphur and ash, and, of course, the calorific value. An ultimate analysis, giving carbon, hydrogen and nitrogen, should occasionally be made. It must be remembered that moisture is not merely a makeweight to be deducted from the value of the coal; it is a positive source of expense, as it has to be driven off before the coal can be ground. In like manner a coal having a given

calorific value and containing much hydrogen is a dearer material than a coal of the same calorific value containing little hydrogen, because the whole of the water produced from that hydrogen has to be raised to the temperature of the exhaust gases, and both the latent heat of water and the specific heat of steam are high. Such practical considerations must be kept steadily in view if cement manufacture is to be economically and successfully conducted.

It will be seen from this summary that the question of fuel for burning cement is of great importance.

CHAPTER IV

MANUFACTURE

THE first step is the preparation of the raw materials so as to bring them into a suitable condition for their combination to form the very complex chemical substance called Portland cement.

In the chapter on raw material it has been shown that, though necessarily chemically similar, the raw materials for cement making may differ very widely physically. It follows that the methods of mingling these materials must be adapted to their physical character. Chalk can easily be reduced to a pulp and so can clay, but limestone and slate, equally suitable as raw materials for Portland cement, need a very different treatment. In the old days of least resistance, soft materials like chalk and clay were mixed in a wash mill with a great deal of water, and the product was fine enough to be burnt into cement quite good of its date. Then, as a monopoly of chalk and clay was impossible, harder substances had to be used. Hence came grinding machinery for raw materials. Before that time grinding was confined to the clinker, and it was thought rather an innovation to grind even soft and wet raw materials. "Wet stones," *i. e.* millstones grinding slurry were, within the author's recollection, somewhat novel and considered of doubtful value. At the present moment no pains are considered too great to reduce the raw materials to the finest practicable condition. The reason is purely chemical. It is no use having a piece of chalk and a piece of clay a mile apart, however much either or both are heated. It is very little good if they are a millimetre apart. Supposing that they were in true molecular contact, their interaction would be easy. Now such intimate contact is not attainable, but the cement manufacturer has to do the best he can to approach it. Hence it comes about that the first step is to comminute the raw materials. When the time comes this comminution will be superseded by the easiest of all methods of mingling such raw materials, namely by fusion. Suppose a

blast-furnace manager were confronted with the problem of fluxing the silica in his ore with his limestone, on the condition that the temperature of operation should not exceed 1200°C ., he would regard it with coldness suitable to that temperature. The problem of the cement-works manager is at present precisely the converse. He must not go beyond the ordinary clinkering temperature. But this is because Portland cement, as now made, contains at the most 65 % of lime, and would be fused and useless at a temperature much exceeding 1200°C . When, however, the proportion of lime is raised to 70 %, a different state of things occurs. The cement can be fused and is perfect. Le Chatelier indicated that such a composition is theoretically sound, and Michaelis proved it experimentally; the author has confirmed his work. It follows that the best way of making perfect Portland cement is by fusion of the two main constituents, because the product will then be homogeneous. To put this method into practice is not easy. The necessary temperature is high, not less than 1750°C ., and this cannot be easily and cheaply attained. There must be enough margin of temperature to allow of the cement being run out of the furnace as easily as blast-furnace slag. As the fused cement is a very basic material (containing 70 % of lime), the walls of the furnace must either be of basic material, such as magnesia, or must be cooled sufficiently to cause the molten cement to set and form a protective lining against itself. There are several ways in which the necessary temperature can be obtained. The most obvious is by electrical heating. It is shown in the section on Fuel that the cost of burning cement by electrical energy is prohibitive save under exceptional conditions, but it does not follow that electrical fusion of cement is out of the question. The operation would take place in two stages. The greater quantity of heat necessary for decomposing the calcium carbonate and bringing the materials to a clinkering temperature would be provided by fuel used in the ordinary way, and when the full clinkering temperature had been reached the material would descend into a zone provided with electrodes by which the temperature would be raised to the fusing-point of the cement and tapped. The fused cement would be granulated by running into water or by blowing steam against the molten jet, very much as blast-furnace slag is granulated or made into slag wool. By this method of comminution the cost of grinding of the raw materials would be saved altogether, and the cost of grinding

of the finished cement would be materially reduced. But an even greater advantage would be the perfect homogeneity and soundness of the product. At present, even with the best and most modern methods of cement mixing and burning, the produce is not strictly homogeneous, and the union of its acid and basic constituents is incomplete. The proof of this lies in the fact that various methods of maturing the clinker—*e. g.* by watering it as it comes from the kiln, by exposing it in heaps for considerable periods and the like—are in use, while steaming and storage of the cement after grinding are in common use for the same purpose. All this would be abolished if the cement were tapped from a furnace in a fluid condition.

With this object in view various inventors have worked on the problem. Probably the nearest approach to success has been achieved by Hurry & Seaman at the Atlas Cement Co.'s Works at Northampton, Pennsylvania. These inventors started on the principle of an ordinary blast furnace for making pig iron. In making certain grades of pig iron the slag is intentionally kept high in lime and may contain between 45 % and 50 % of calcium oxide. When the lime content is raised and approaches the lower limit for Portland cement, which may be taken as about 60 %, the fusibility of the material decreases. It occurred to the inventors to raise the temperature of the furnace by working it under pressure—say 20 lbs. per square inch. Beginning with an ordinary slag containing some 45 % calcium oxide, they gradually altered the "burden" of the furnace by increasing the lime content, hoping that at the increased pressure the Portland cement itself, containing 60 % calcium oxide or over, might be fused. The idea is good and ingenious, and a considerable number of experiments were made which seemed likely to be fruitful, but for various reasons, not directly connected with the idea itself, they were abandoned, and as far as I know have not been resumed. Certainly the notion is worthy of more extended trial.

Another method has been suggested and its possibilities most carefully examined. It is to use a furnace of the blast-furnace type fed with air enriched by oxygen. As is well known, air is liquefied in large quantities, and the liquid nitrogen and oxygen are fractionated to any desired point. Both gases are industrially valuable, but there is a surplus of supply over demand for the oxygen, which, of course, is necessarily produced in a definite relation to the nitrogen. It follows that a new outlet for the

oxygen would be welcomed by the manufacturers. The plant needed for making liquid oxygen in large quantities is relatively costly and requires a considerable amount of power to run it, and although by modern methods oxygen can be and is made at prices which would have been regarded as impossibly low thirty years ago, yet it is still an expensive commodity compared with common air. It was hoped that by working on a large scale and cutting down the amount of oxygen-enriched air to as low a point as was consistent with attaining the fusing-point of a cement mixture containing about 70 % calcium oxide, which was provisionally assumed to be in the neighbourhood of 1750°C. , i. e. about the fusing-point of platinum, the use of oxygen for fusing cement might be commercially practicable. Careful calculations covering every essential factor of such an undertaking were made, but the result was not sufficiently encouraging to warrant immediate action. A substantial cheapening of the cost of oxygen would alter the whole situation, and in my opinion the manufacture of cement by fusion in a super-blast furnace will ultimately be an accomplished fact. Just prior to the war I had the advantage of a consultation with Dr. Linde, and he agreed that no obstacle existed except the cost of the oxygen made by his process, and this was within sight of practicability.

Reviewing what has been stated above, it may be said that at the present date no cement is made at any other than a "clinkering temperature." The term is employed because there is no more precise definition. Evidently it will vary with the nature of the mixture of raw materials, which must be brought to a temperature at which the product is plastic so that interaction may occur short of fusion, which, with the present limitation of lime content, would produce something little better than a slag.

Taking, then, the Portland-cement industry as it is and not as it may be in the future, the steps in its manufacture are described below.

The nature and composition of the various raw materials commonly used for making Portland cement have already been described in a preceding section. As previously mentioned, the industry began with chalk and clay as the raw materials. The chalk was obtained by quarrying, and being soft, hand labour was universally employed. The material is hewed down and conveyed away by small trolleys to the wash mill. The clay,

taken from an estuary like that of the Medway, is dug or grabbed out, put into barges and conveyed to the works, which are naturally situated at the chalk quarry, the chalk being much the larger part of the raw material needed.

There is, of course, a continual tendency to decrease hand labour as much as possible and to use steam navvies and to haul by power, but the nature of the material renders working so easy that, provided a quarry is well laid out, the cost of getting is very moderate. It will be understood that the life of a chalk quarry is limited by the height of the water level in the chalk, and that when this is reached quarrying in the ordinary manner is automatically stopped, although there may be an ample supply of chalk below water level. As this may mean failing to win a considerable quantity of valuable material and being forced to go further afield to feed the works, efforts have been made to work below the normal water level. A very notable case occurred a few years ago. A quarry had been worked down to water level, and there was an excellent demand for more chalk from that site. It was therefore decided to go deeper and to keep the water down by pumping. The necessary pumps were installed and the work proceeded with. There appeared to be little difficulty in keeping the in-coming water under control, but the pumps began to show signs of corrosion and the chalk of discoloration. The injury to the pumps was serious enough, but the discoloration of the chalk was of far greater moment, as a large part of the output was used for making whiting. The cause was discovered without much difficulty. Next to the chalk quarry was a sulphite pulp works, from which a large quantity of spent sulphite liquor found its way into the quarry. This sulphite liquor made an excellent pabulum for *beggiotoa alba*, which has the faculty of thriving in liquids rich in sulphur, and reducing the sulphur compounds to organic sulphides and to sulphur itself. These acted on the traces of oxide of iron in the chalk and converted them into ferrous sulphide, which is black. Hence the discoloration of the chalk. Having done this mischief, the sulphite liquor passed on, became partly oxidised on its way, and attacked the metal of the pumps. Costly litigation ensued, with the usual disastrous results to both parties. Thus by a purely fortuitous circumstance an idea excellent in itself and tried on a large scale and in a practical way failed to obtain success. This is the more to be regretted as, had the notion proved successful in this instance, it might well have

been applied in similar instances where there was no reason to fear contamination of the chalk or corrosion of the pumping machinery.

In the earlier stages of the cement industry in this country the mixture of chalk and clay prepared in the wash mill of the period¹ was made with a large quantity of water so that it might flow. The very thin slurry, containing perhaps 75 % of water (that is, three times the weight of the raw materials), was run to any required point without difficulty, but as this large amount of water had to be evaporated before the slurry was burnt the cost of fuel was excessive. Accordingly the fluid material was run into large reservoirs, called "backs," and there allowed to subside, the water being drawn off from time to time, and the sludge (which still contained much water) dug out and carried to the kilns. It occurred to some of the thinking manufacturers of that date (about thirty years ago) that there was a risk of segregation, as it was recognised that, although the specific gravity of the two materials did not differ much, yet their rate of settlement might differ materially. A direct test was made which came into the author's purview. A column was cut from the semi-solid material in the "backs" and the top and bottom parts analysed. It was found that there was no appreciable difference in the composition of the top and bottom of the column, and it was concluded that the slurry could be used with safety after months of deposition. This excellent test of the capabilities of the old process is a fairly good instance of what can be done by men trained in a rule-of-thumb school, but having natural sagacity, if only they will avail themselves of current knowledge.

The next step in the old wet process was to grind the chalk and clay as the mixture issued from the wash mill, between ordinary millstones. The product was still sufficiently fluid to be pumped and was distributed on drying floors, from which it was removed by hand labour when it had been thoroughly dried. The heat necessary was provided in the early stages of the industries extraneously, and a great advance was made when the waste heat of the cement kilns was employed for drying the slurry. This was done in the type of kiln shown

¹ The early wash mills were a somewhat cruder form of the modern wash mill, a description of which is given below. It is sufficient to say here that the wash mill is a machine for mixing soft raw materials with water to a slip or slurry in such a way as to leave the coarser particles behind and produce a material fluid enough to be pumped.

in the figure (Fig. 4). By permission of the Institution of Civil Engineers, before which body a paper by my late partner, Mr. W. Harry Stanger, and myself was read in February 1901, I reproduce this and similar records. It will be seen that the gases from the kiln pass through a flue in which the slurry is spread. The whole affair is rather primitive, as the slurry is immobile and the mode of drying is not systematic. In the paper referred to above the following statement is made—

“The kiln is a brickwork structure about sixteen feet in diameter and eighteen feet in height, having a grate at the

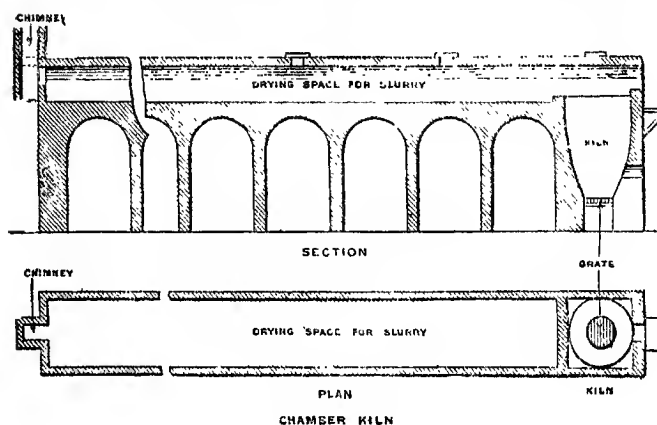


FIG. 4.

bottom and opening into a long, wide, horizontal flue, in which is run the slurry to be dried by the waste gases. The fuel used is coke, which is loaded into the kiln interspersed with the dried slurry; the quantity required is 40 % to 50 %, reckoned on the weight of clinker produced. Coke is not only a relatively costly fuel, but it is liable to sudden and artificial fluctuations of price, a tendency highly inconvenient to the cement-maker. The labour needed for loading and drawing the kilns is very heavy, and the clinker produced is far from uniform, often containing much under-burnt material, which needs to be picked out before the clinker is ground. A kiln of this class of average size will need five days to six days for a complete trip, and will not produce more than about 35 tons of clinker per week.”

This is perhaps the best attempt which has been made to convert a rough method of burning into something having a scientific basis using wet raw materials, and it must always be remembered that the whole basis of the huge Portland-cement industry is purely English, and rests on the rudimentary knowledge of the time of Aspdin.

This method of drying and burning has long been superseded for wet raw materials, but when dry raw materials were concerned there was some reason to think that the fixed kiln might hold its own. Appended is an excerpt taken from the paper cited above.

“When dry materials—*e.g.* shale and limestone—are used, some form of continuous kiln is generally employed. The materials are finely ground, intimately mixed and damped sufficiently to enable them to be moulded into rough bricks. These are burnt in ring- or shaft-kilns. The ring-kiln of the Hoffmann type is largely used in this country in the manufacture of bricks, but is rarely employed for cement. It is economical of fuel, needing only about 15 % to 20 % on the weight of the clinker produced, but requires a large amount of fairly skilled labour in stacking the bricks of cement material into the chambers of the kiln, and in regulating the firing by feeding fuel into the spaces left between the stacked bricks; it has also to be unloaded by hand. The necessity of regular stacking of the material to be burnt makes the Hoffmann kiln less suitable for treating material such as cement, which becomes deformed when hot, than for burning building-bricks and the like, which retain the regularity of their shape.

“The Dietsch kiln is a typical shaft-kiln, and is largely and successfully used for burning cement.

“As shown in Fig. 5, it is a continuous kiln, having a feeding-door at the base of the stack, a burning-chamber and a cooling-chamber through which the material to be burned successively passes. It is economical of fuel, using 15 % to 20 % of the weight of the clinker produced, but is costly in labour.

“Both the Hoffmann and the Dietsch kilns can be used for wet raw materials, but they require supplementary drying arrangements by which the slurry may be dried sufficiently to allow of its being moulded into bricks. The amount of fuel necessary for drying is usually somewhat greater than that needed for burning, so that the total amount of fuel required—

viz. 35 % to 40 % on the clinker—is not much smaller than that needed for chamber-kilns, but a cheaper kind of fuel can be used, namely small coal.

“The principle of continuous working is so attractive, on account of its economy in fuel and its increase of output per kiln, that it has been embodied in various other forms of kiln. These are in general vertical cylindrical shafts not unlike a running lime-kiln, but usually with a flue or chimney at the upper end and loading-doors at the base of this flue. The clinker is drawn at the bottom, where there is usually some kind of removable grate. In one

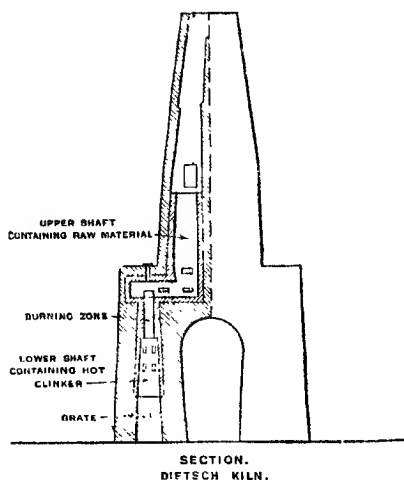


FIG. 5.

kiln of this class a blast of air is blown in at the base of the kiln. The charge is regulated so that the mixture of coke and cement material is in full ignition at a point about one-third of the way down the kiln, its products serving to heat the raw material in the upper part, and the hot clinker in the lower part yielding its heat to the incoming air. Kilns of this class are economical of fuel, but as a rule require the use of coke instead of small coal, and need a good deal of skill in loading. The hot plastic clinker is liable to stick to the walls of the kiln, causing the charge to hang; this not only hinders the proper working of the kiln, but also acts on the lining and hastens its destruc-

tion. Unless skilfully worked these kilns are apt to yield a good deal of under-burnt clinker which has to be picked out.

"The quantity of clinker produced by these different classes of fixed kiln varies considerably with local circumstances, but may be stated in round figures as follows: Chamber-kiln, 35 tons per week; Dietsch kiln, 70 tons per week; Schneider kiln,¹ 70 tons per week; Hoffmann kiln, 28 tons per week for each chamber.² With all these varieties of fixed kiln the amount of labour needed for handling the raw material and clinker is large, whether the kiln be continuous or discontinuous. Moreover, kilns of the continuous class, when wet raw materials are used, require an elaborate drying-plant to prepare the raw material before it is fed into the kiln to be burnt. In whatever class of fixed kiln it is produced the clinker is irregular in quality, containing a good deal of imperfectly burnt material; unless this is picked out most carefully, sufficient under-burnt material remains to impair the quality of the finished cement in a serious degree. Finally, the finished cement needs to be matured by storage before it can be used with safety for important work."

After some nineteen years there is little to add to or retract from what was then written.

There has been a steady decrease in the number and importance of fixed kilns, whether for the treatment of raw materials wet or dry. The writer well remembers a visit to Aalborg in the north of Denmark, where the raw materials are chalk and clay, which latter is rather silty. At the time of that visit the idea of a fixed kiln was so predominant that only tentatively was the rotatory kiln being introduced, and this is less than twenty years ago. To put it shortly, the fixed kiln is dead.

For all that, its history is interesting, and therefore has been included in this book. From the time when it was found in this country by "a crew of patches, base mechanicals"—that is to say, the folks who knew and were not afraid to make blundering trials—that chalk and clay would make cement by being burnt together, there has been a continuous advance.

Modern manufacture is much the same all the world over,

¹ This is a kiln of the continuous cylindrical shaft type last mentioned.

² A ring-kiln of fourteen chambers each, having a capacity of 40 tons, will give 560 tons of clinker for a complete round trip, which will take about ten days. This represents an output of 56 tons per day, or 392 tons per week for the whole kiln, *i. e.* 28 tons per week for each chamber.

such differences as exist arising from the different nature of the raw materials employed and the variation of local conditions.

Fig. 6 shows diagrammatically the methods employed to prepare the various raw materials for burning. It will be more convenient to consider the different methods as a whole, pointing out those operations which differ materially and those which are identical.

PREPARATION OF RAW MATERIAL

It will be assumed that the raw materials are chalk and clay or marl which can be *washed* to a slurry. It is true that dry raw materials, such as limestone and slate, are *ground* with water to a fluid consistency, but for simplicity it is best to deal here solely with the former class, it being understood that what is said of them holds also with regard to raw materials naturally hard and dry but intentionally reduced to such a state that they can be handled as a fluid material, and that once that condition has been obtained their original state as found in nature is not of material importance.

Taking the chalk and clay as typical wet raw materials, the first step in manufacture, as briefly mentioned above (footnote on p. 55), is to mix them in a wash mill. The proportions must be such as to give a cement containing 62 % to 63 % of lime and with ordinary chalk and clay this corresponds approximately with a content of about 75 % of calcium carbonate (CaCO_3) in the mixed raw materials when dried. These figures naturally vary somewhat according to the percentages of substances other than actual CaCO_3 in the chalk, with the composition of the clay and with the ash of the fuel, and are matters for control by the works chemist. Of greater importance is the percentage of water in both raw materials, which may vary considerably. But as a rule fluctuations in masses of plastic material such as chalk and clay, nearly or quite saturated with water, do not take place rapidly, and it is usually sufficient to assume an average content. Using this as a basis, the proper quantities of chalk and clay are weighed into the wash mill and then mixed, final adjustment being made in a correction of dosage tank.

By the kindness of Messrs. Smidth of Copenhagen and London I am able to give the latest form of wash mill in plan and section

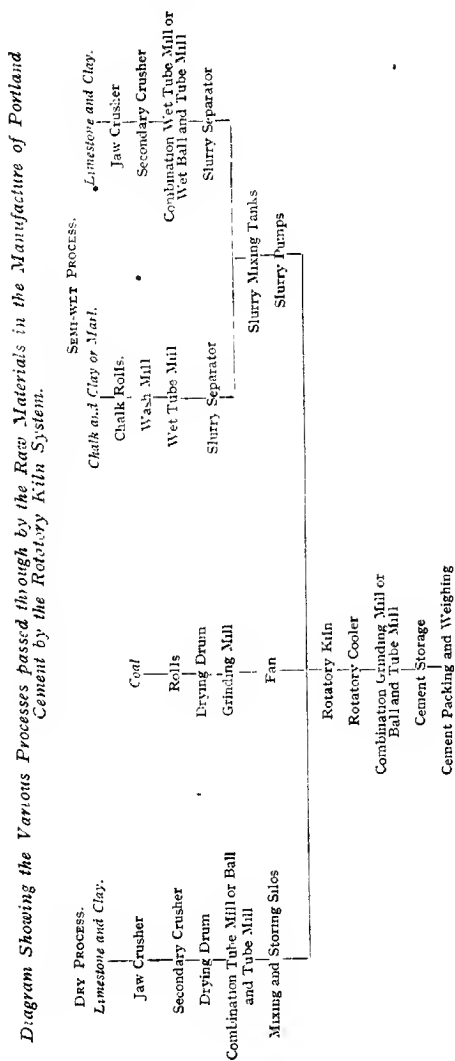


FIG. 6.

Figs. 7 and 8, which, though identical in principle with the earlier forms, shows considerable development in design and efficiency.

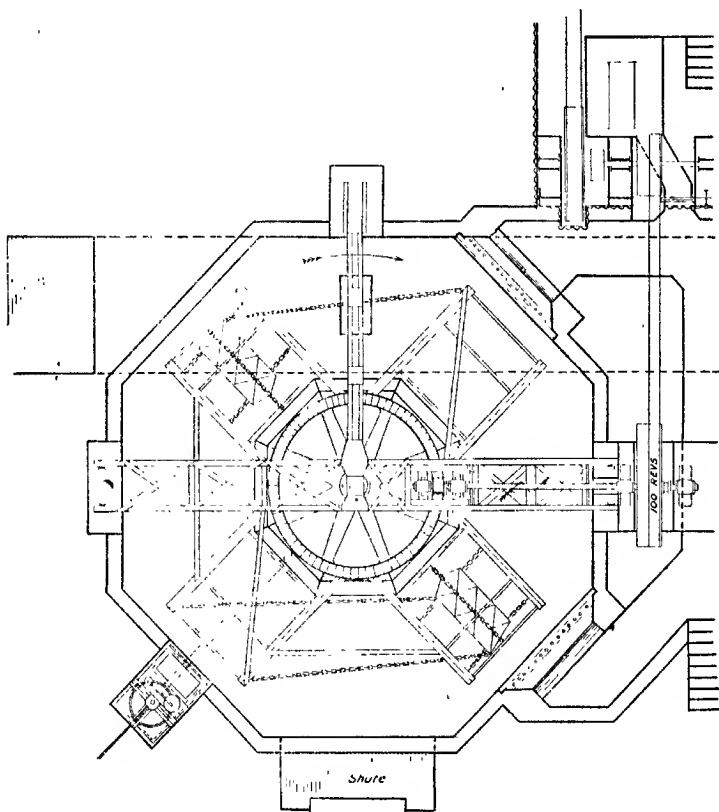


FIG. 7.—Modern Wash Mill (plan).

It will be seen from these that a wash mill is a large cylindrical tank usually made of concrete, with a vertical shaft carried on a concrete pillar which fills the middle of the tank and leaves an annular space between itself and the walls of the tank. The shaft carries horizontal arms from which harrows are slung by means of chains, as shown in the section. The teeth of the

harrow are attached to the horizontal bars, which in turn depend from the chains above mentioned. This arrangement allows the harrow slung as it is to hang loose so that its teeth (the vertical bars) strike any solid mass in the tank with a flail-like blow, yielding and passing on if the lump is not immediately smashed. The central shaft revolves with considerable velocity, and the loose hanging bars speedily break up the masses of chalk and clay as they are fed in. Stones and flint are gradually deposited, as well as a good deal of the sand; a further quantity of the latter is caught by screens at the outlets of the wash mill; both stones and sand are, of course, removed from the wash mill

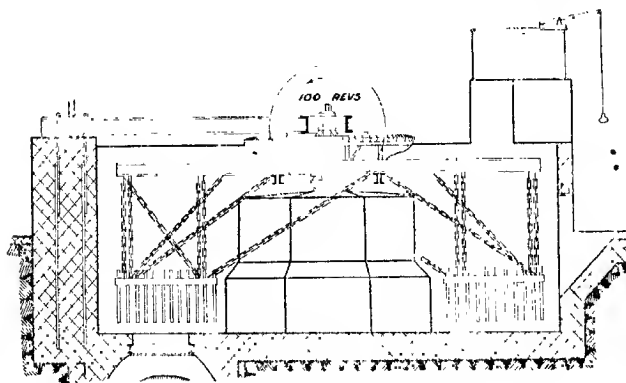


FIG. 8.—Modern Wash Mill (vert. sec.).

from time to time. The result is that a slurry or slip fairly uniform and fine is obtained.

As mentioned above, the proportions of chalk and clay are finally adjusted in a dosage tank, samples being drawn and analysed and the requisite addition made of the one material or the other.

A dosage tank is merely an agitator with a vertical spindle carrying a horizontal framework to which are attached vertical bars or paddles so as to stir the mixture thoroughly and continuously. The whole arrangement is not unlike a wash mill, but as its main function is not to break up lumps of raw material but to form a uniform mixture of known composition, the vertical bars are attached rigidly to the framework instead of swinging loose as in the wash mill itself.

The finely-ground slurry of correct composition is now conveyed to the bulk mixing or storage tank. These tanks vary in design, but the illustration shown in Fig. 9 may be taken as typical. It consists of a tank built of concrete or brick provided with stirrers to prevent any settlement taking place.

Another maker's system of handling wet raw materials is shown in Fig. 10, which is almost self-explanatory. The wash mill is of the usual type and the slurry is pumped into a separator marked "Trix," which is a sieving machine on a centrifugal principle, from which the coarser particles are returned to the wash mill. The bulk of the slurry passes into a tube mill and then into a tank where any necessary correction of composition

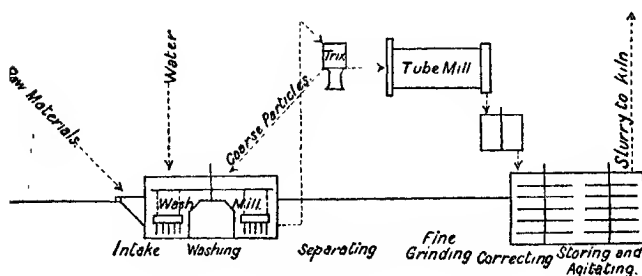


FIG. 10.

is made. Thence it passes to a large storage tank provided with agitators, and out of this it is pumped to the kilns.

When the raw materials are hard but are to be delivered as a slurry to the kilns, the plant shown in Fig. 11 is suitable. The raw materials are crushed, elevated to hoppers and fed into a form of ball mill without screens. Water is added here and the raw materials are ground wet. They then pass through a "Trix" separator such as that used for soft raw materials, and the coarser particles returned to the kominator. The fine part of what is now in effect slurry passes to the tube mill, thence to a correction tank and to a large storage tank, precisely as in the case of the wet raw materials. From this it is pumped to the kiln. In short, save for the crushing and wet preliminary grinding in the kominator, the process is the same as that used for raw materials naturally wet. The whole arrangement is shown diagrammatically in the sketch.

In ordinary practice the large capacity of the slurry tanks and

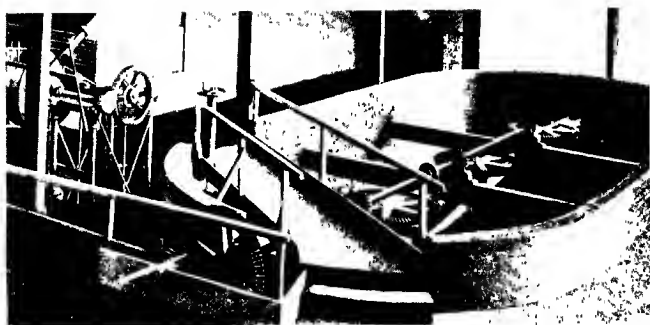


FIG. 9.- Slurry Storage Tank

tube mills, together with the final storage tanks, is sufficient safeguard for proper admixture, but in some cases additional precautions may be desirable. This emphasises the absolute necessity of thorough admixture of raw materials before they enter the kiln, and it is not too much to say that unless this is accomplished the manufacture of perfect cement which will need no quenching, storage or aeration is impossible. This is one of the most cogent arguments in favour of the blast-furnace method of burning which has already been touched on, as then the mixture by fusion is complete.

The slurry thus prepared and of proper composition contains about 38 % to 40 % of water, according to the nature of the

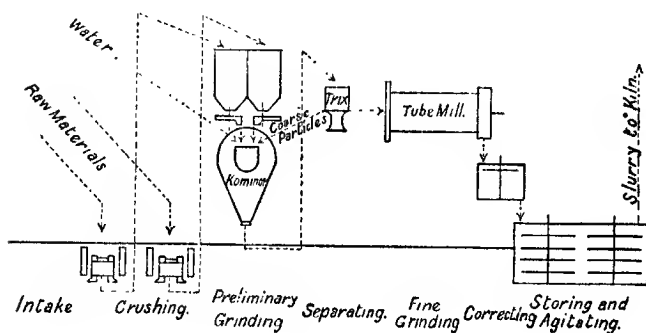


FIG. 11.

raw materials. If the clay is silty the proportion of water will be smaller, and there are also clays of a peculiarly tenacious character which require considerably larger quantities of water to reduce them to a pulp which will flow. The whole question must be decided experimentally in each case, it being borne in mind that, provided the slurry can be dealt with as a fluid mixture without clogging channels or pumps, the less water the better.

It was early recognised that in spite of all care in mixing in the wash mill and in the separation of the coarser particles therein, the slurry as it left the wash mill was relatively coarse. Indeed, formerly it contained pieces of chalk as large as peas, easily discernible when the slurry was dried on the drying floors of the old fixed kilns. It can readily be understood that the presence of such pieces, and even those which were much smaller, would

have a most injurious influence on the quality of the cement, especially in respect of soundness, and it is not too much to say that the suspicion with which many engineers regarded Portland cement, even as recently as thirty years ago, was based on want of soundness arising from this cause among others. In consequence an attempt was made to meet the difficulty by wet grinding. It must be remembered that at that date the standard method of grinding in the cement trade was by ordinary mill-stones, and that these had been employed from the beginning of the industry to grind the clinker; it was therefore an easy step to run the slurry through similar pairs of stones, and the step was undoubtedly a great improvement. It may properly be asked how it was possible to make even tolerably sound cement before wet grinding was introduced. The answer is simple. In the old type of fixed kiln the coarsely ground raw material remained at the clinkering temperature for several days, and an approach to full combination of the acid and basic constituents of the raw materials was made by their interaction whilst semi-plastic for such a period: exposure for about an hour, as in modern practice, would not suffice to deal with pieces so coarse, and in consequence the modern cement-maker aims at preparing a slurry giving a residue not greater than 3 % to 4 % on 180 \times 180 mesh sieve, and practically no residue on 76 \times 76 mesh sieve.

When the grinding of clinker in ball and tube mills (*q. v.*) became an established practice, similar machinery was adopted for wet grinding. A ball and tube mill plant varies but little in principle, though in detail it differs according to the design of the various makers of cement plant. A ball mill (known under various names) consists of a fairly short drum lined with hard steel plates and containing a number of hard steel balls of different sizes. It is rotated on a horizontal axis, and as it rotates the raw materials mixed with the steel balls travel up the side of the drum and continuously fall back, the raw materials being pulverised by the joint pounding and rubbing action of the balls. It is usually fed at the centre and discharges at the periphery through holes in the steel plates and screens exterior to the plates, though in some types both feed and discharge may take place centrally.

The tube mill is much longer than a ball mill and is lined with steel plates or siliceous blocks or bricks. The grinding is effected by steel balls or flint pebbles, which act much in the same way

as those of a ball mill. The material to be ground is fed in at the axis of the mill through a trunnion, travels the length of the mill and is discharged through a trunnion at the other end. Following these general statements is a description in some detail of the various machines used for reducing cement materials to a sufficiently fine powder.

In the case of wet raw materials there is no preliminary treatment at the quarry, but with dry raw materials some form of crusher or stone breaker must be employed, and it is usually convenient to run this at the quarry. This applies to both limestone and shale, as transport by whatever means is easier when the material is of relatively small size, and because the two substances have ultimately to be mixed intimately, and as power is certainly available at the works, the final grinding can be carried out there.

Getting the limestone and shale often involves blasting, but this is an ordinary quarrying operation and need not be dealt with here. What is of more importance is the need to quarry in such a way that the layers of intercalated matter and sand and similar material are avoided as far as possible, and that the clean shale and limestone are obtained. Some hand picking is generally necessary, and strict control of the material delivered to the works is absolutely essential. In the case of the shale too much dependence must not be put on local opinion, which is apt to be misled by difference of colour due to the slow weathering of the shale and the oxidation of the iron which it contains. It may well be that layers of shale, one blue and one brown, have substantially the same composition. What is more important is the amount of moisture in the shale. To sum up, first there is the question of transport: this, though important, is not pre-eminent; next is the question of handling, which is of great moment; and, finally, in a works using shale and limestone by the dry process, is the very important question of thorough drying.

Although the plant used in cement manufacture can all be referred to a comparatively few types and described in general terms, yet it has been thought well to give examples of various machines, drawings of which have been provided by well-known makers.

CRUSHING AND GRINDING

For hard, dry raw materials crushers are naturally necessary. It must be understood that the fineness of crushing is largely

dependent on the type of grinding plant which is used, the function of the crusher being only preparatory. There are several types of these, which are described and illustrated below. The commonest are the Gates crusher and the Blake crusher. The Gates is a rotating crusher of the coffee-mill type.

One example of this type of mill is shown in Fig. 12, viz. the Heclon crusher made by Hadfield. The material is fed through a hopper and falls between the toothed faces of the cones 7 and 27, where it is crushed by the revolution of the inner cone No. 7, and falls down the shoot No. 29. The crushing effect is increased by a gyratory motion imparted by the cone by the special gearing at the base. The names of the individual parts are here given and this will enable the improvements in this crusher to be seen.

- | | |
|----------------------------------|--|
| No. | No. |
| 1. Bottom Shell. | 20. Outer Bush. |
| 2. Bottom Plate. | 21. Lower Ball. |
| 3. Concave Casing. | 22. Lower Ball Socket and Screw. |
| 4. Hopper and Spider. | 23. Lock Nut. |
| 5. Main Shaft. | 24. Spider Bush. |
| 6. Cast Steel Centre. | 25. Spider Cap. |
| 7. "Era" Manganese Steel Mantle. | 26. Spider-arm Shields. |
| 8. Central Shaft. | 27. Lower Concaves. |
| 9. Ring Nut. | 28. Upper Concaves. |
| 10. Upper Ball Socket. | 29. Shoot Lining Plates. |
| 11. Upper Ball. | 30. Main Shaft Wearing Ring. |
| 12. Eye Bolt. | 31. Bevel Pinion. |
| 13. Locking Screws. | 32. Countershaft. |
| 14. Ring Nut Locking Pin. | 33. Countershaft Bearing Cap. |
| 15. Dust Ring. | 34. Countershaft Bearing. |
| 16. Lower Dust Collar. | 35. Belt Pulley. |
| 17. Dust Collar Carrier. | 36 and 37. Countershaft Wearing Rings. |
| 18. Bevel Wheel and Eccentric. | 38. Washer for Adjusting Screw. |
| 19. Inner Bush. | |

Blake crusher.—The simplest form of crusher is the jaw crusher, shown in Fig. 13. It consists of a pair of jaws, faced with hard steel plates. One jaw is fixed, and the other movable. A cam shaft is connected with the movable jaw, by means of toggle plates, and causes it to approach to, or recede from, the stationary jaw.

Another example is the roller crusher, shown in Fig. 14. It consists of toothed rollers working against each other, the material being fed in by a hopper between the two rolls. In order to prevent the breakage of the teeth a strong spring is provided to allow of the rolls parting, should a large lump of unusually hard material find its way into the feed.

Another form of crusher is the Hecla Disc crusher. Fig. 15 shows it in section.

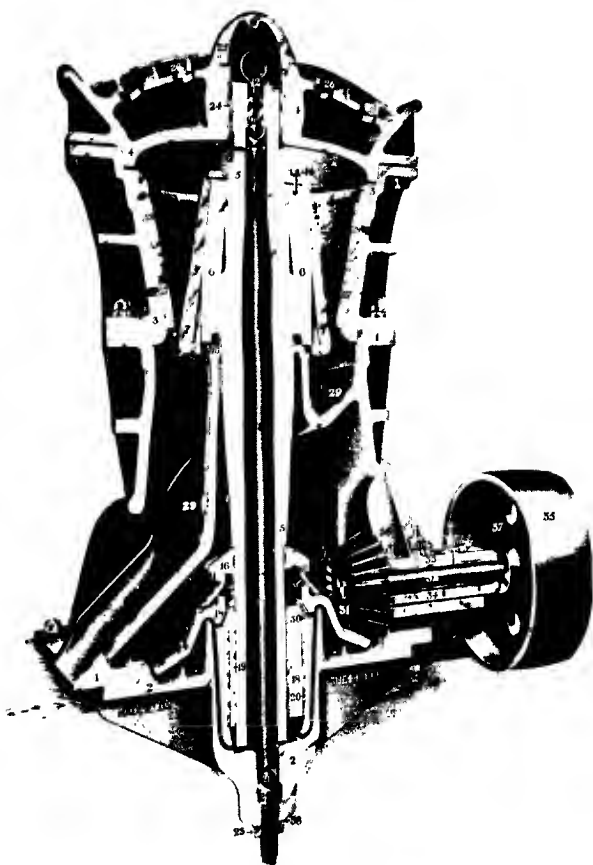


FIG. 12 —Heclon Rock Crusher.

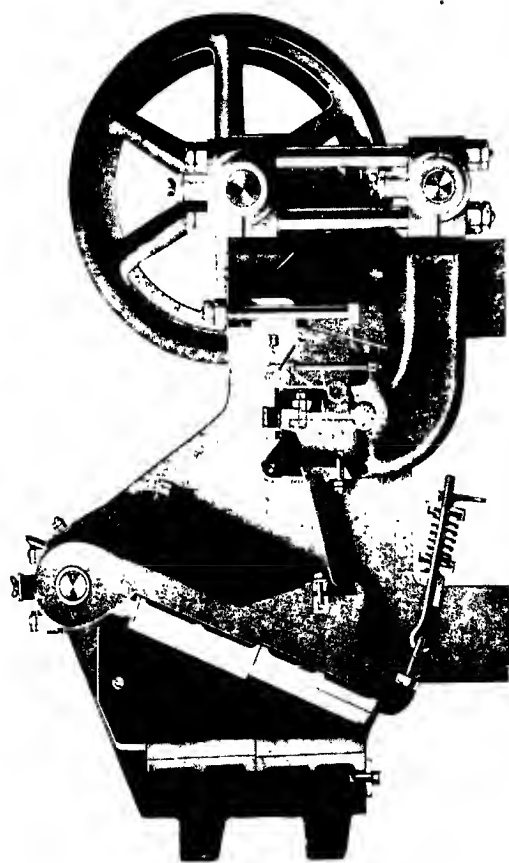


Fig. 13—Blake Crusher

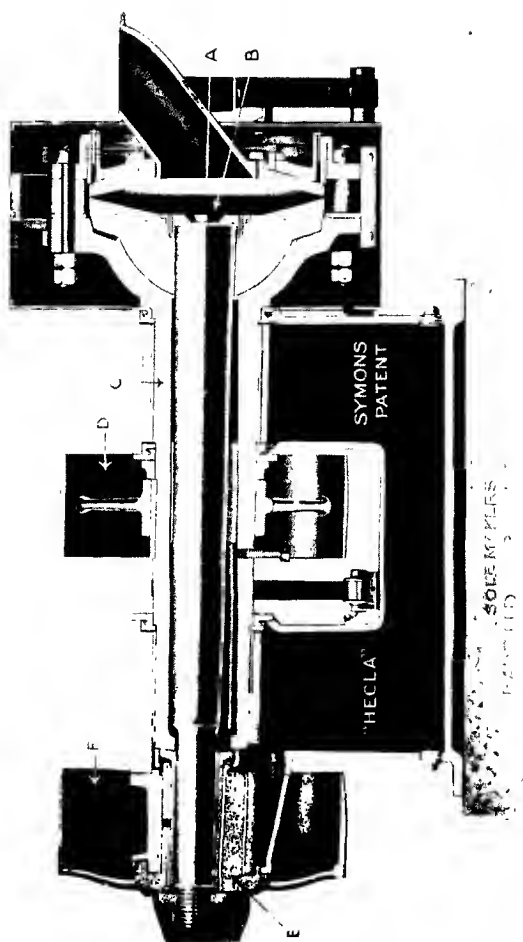


FIG. 15.—Hecla Disc Crusher

The two discs *a* and *b* are held in place by two shafts, one of which is hollow and contains the other. The large ball-and-socket connection of the shafts allows their axes to be set at an angle to each other.

The outer disc *a* is held in a cap firmly fastened to the bell-shaped end of the hollow shaft *c*, and is driven by the belt-wheel *d*. The inner disc *b*, supported by the half ball and solid shaft, inclines to rotate with the disc *a*, though not positively driven when the machine is running empty. When, however, stone is introduced between the discs, they both rotate together in the same direction, at the same speed, affording the crushing action peculiar to this type of crusher.

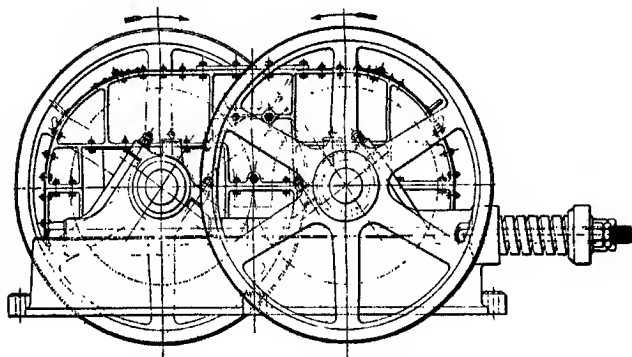


FIG. 14.—Roller Crusher.

This crushing action is quite independent of the eccentric *e*, and would be carried on if the latter remained at rest. This eccentric comprises the hub of the pulley *f*, which is driven in a direction opposite to that of the pulley *d*. The function of the eccentric is to increase the rapidity of the crushing action, by the more frequent closing of the discs. In other words, the outer end of the solid lever shaft is carried around in one direction by the eccentric *e*, while both shafts are rotating together in the other direction.

The two shafts and discs attached rotate at the proper speed to force the feed and fling out the product, while the rapidity of the crushing movement is increased by the eccentric to afford great capacity.

The question of grinding is of the highest importance in cement manufacture, both from the aspect of economy of power and from the view of the quality of the cement. It is therefore desirable to give a few details both of the machines and of their proper use. I have to acknowledge the use of photographs (Figs. 16 and 17) of a kominor by Messrs. Smidth which show both the feeding arrangements, the disposition of the balls and the mode of discharge. The following is Messrs. Smidth's

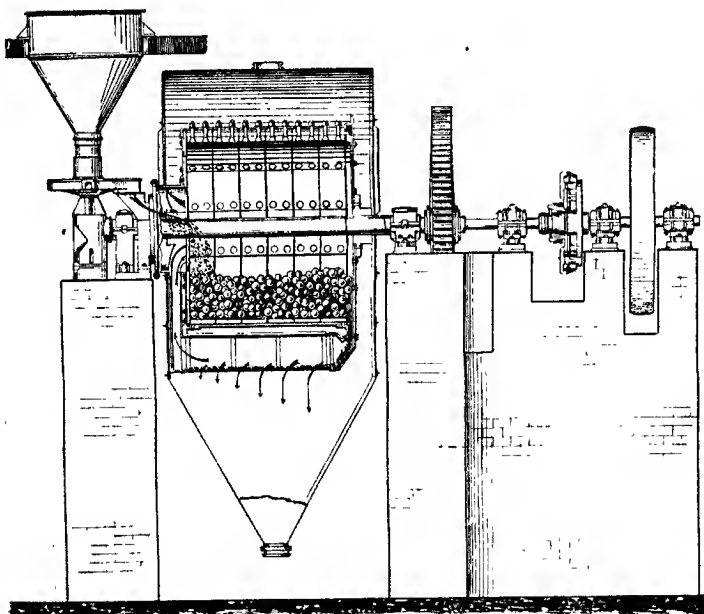


FIG. 16.—Kominor.

description of the functions of the machine, which is not only worth reading on that account, but because it enunciates some general principles in a clear manner.

“Starting from the view that economical grinding is merely making surface at the least expenditure of power and upkeep, we have found it of the utmost importance to always distinguish between crushing, granulating and pulverising. In the crushing process you are dealing with material of comparatively small

surface. Material entering stone crushers or stone breakers may be of any size. The material entering preliminary grinders or granulators should be ground down to one inch to three inch diameter; leaving the preliminary grinders it should be ground fine enough to pass a No. 20 mesh sieve.

“ Finally, the material for the fine grinders should be preliminarily ground to pass a No. 20 sieve and leave the fine grinders to grind down to the desired fineness.

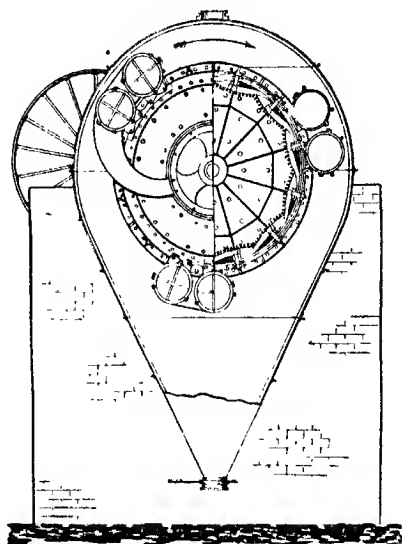


FIG. 17.—Kominor.

“ The surface of the particles leaving the preliminary grinders is many thousand times larger than the surface leaving the crushers, and the surface of the particles leaving the fine grinders is again many thousand times larger than the surface of the material leaving the preliminary grinders.

“ The machinery to be arranged for the three different operations must be of different construction to treat economically the different materials supplied. As, further, the ‘grindability’ of two stones of the same chemical composition varies as much as 100 %, we have found it very desirable to be able to build up our mills from various units.

"An important difference between the ordinary ball mill and the kominor is that the kominor has no perforations in the lining in the track of the grinding balls. In the ball mill the grinding material is discharged through the perforations in the grinding plates, and such perforations being subjected to the pecking action of the balls are accordingly closed and the output is progressively decreased.

"The fastax screens are a great advantage compared with the old conical screens, as they permit of easy and quick inspection of the screens and the bolts holding the grinding plates in position. When necessary to repair the screens any of the screens may be easily removed, and by having spares at hand substitution may be quickly made, reducing the time for changing the screens to a few minutes.

"Both the kominors and the fastax screens are made to our patented designs."

It cannot be stated too clearly that on the proper comminution of cement raw materials the quality of the finished cement depends in so large a degree that all methods to secure this end are worth attention, and have received it to a point when something approaching perfection has been attained.

A typical ball mill by Allen of Sheffield is shown in Fig. 18. It will be seen that the ball mill is a drum lined with perforated metal plates, which are stepped as shown. Outside this is a screen, and the coarser parts drop back into the mill.

A good illustration showing the general appearance, as distinct from structural details, of a tube mill is given below, Fig. 19.

Fig. 20 shows a tube mill for dry grinding. The feed is through a trunnion *a* giving into the tube *b*, which is lined with hard steel plates *c*. It also shows an arrangement marked *d* for the discharge of the material. This consists of vanes *e*, which lift the ground material and discharge it through the cone *f* into the discharge trunnion *g*. In this particular mill the product is passed through the screen *h*, the fine particles being delivered at *i* and the coarse at *j*, to be returned and re-ground.

It will be understood that the grinding arrangements for dry raw materials and for clinker are very similar, and in many works the one is almost a duplicate of the other. The following description of a compound ball and tube mill (Fig. 21) may be taken as applying to both.

The dry raw material, or the clinker, is fed in at A through

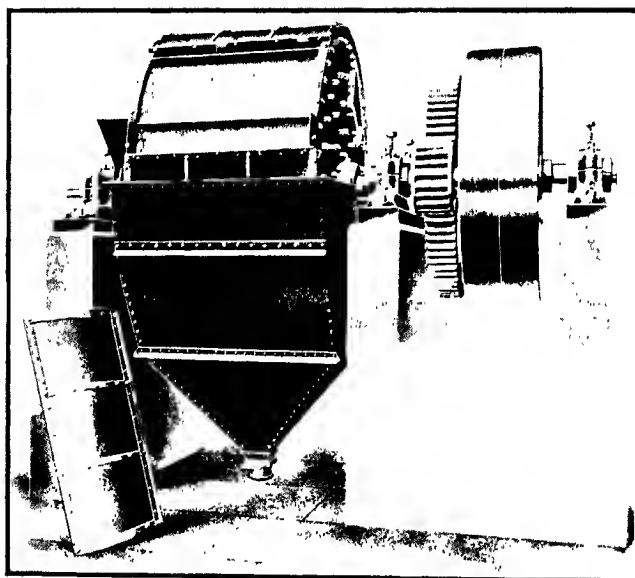


Fig. 18 - Ball Mill

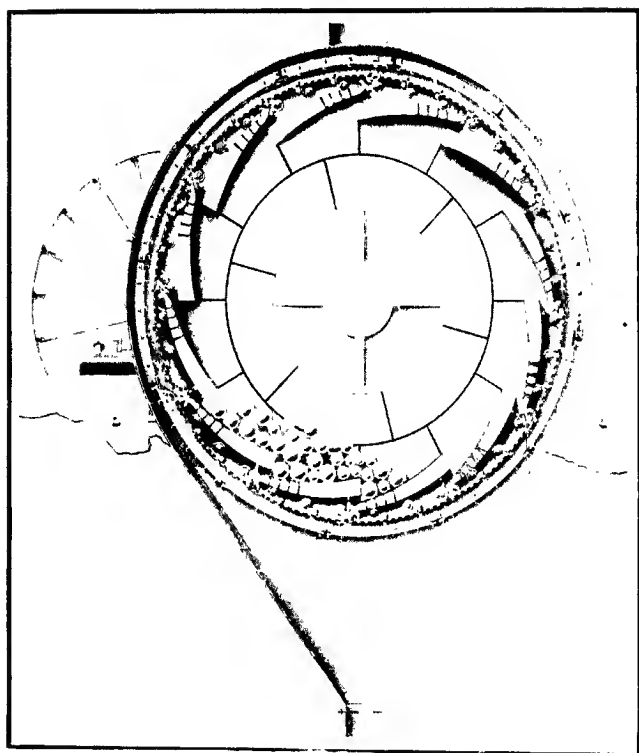


Fig. 48 - Ball Mill. (Section)

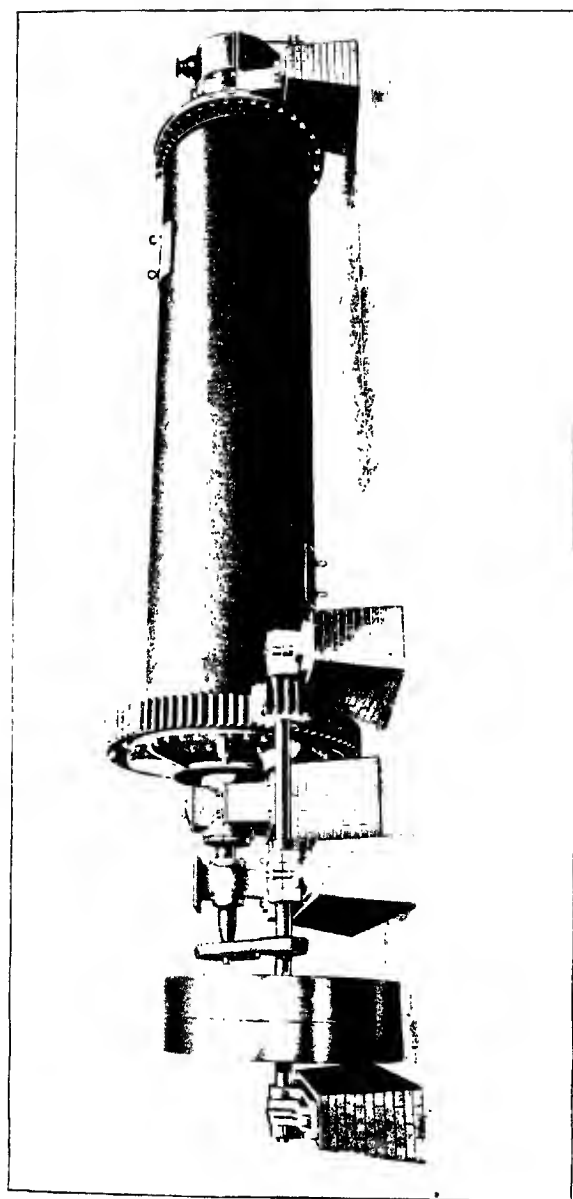


Fig. 10- Tube Mill.

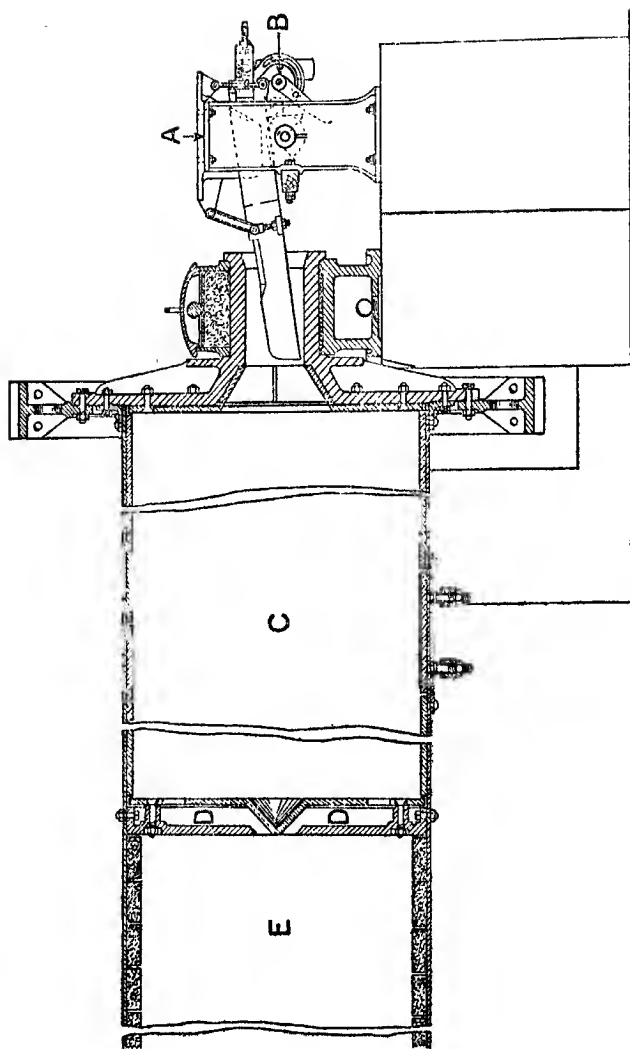


FIG. 21.—Compound Mill.

a tube provided with a percussion arrangement B to avoid holding up and to make the feed regular. It passes through a trunnion into the first chamber of the mill marked C, which is charged with steel balls, and lined with steel plates: the material passes through a diaphragm plate D with taper slots into the finishing chamber E, which is lined with siliceous blocks and loaded with flint pebbles.

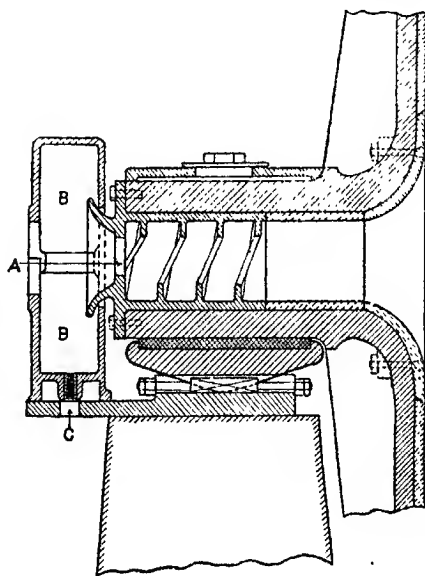


FIG. 24.

An improved form of compound mill is shown, with section, in Fig. 22. In this type of mill the screen is placed in such a position as to be readily accessible.

When dry raw materials are used the modes of feeding are, of course, of different kinds. One of them, the table feed, is shown in Fig. 23. The material is fed in at *a* on to the revolving table *b*. The feed is regulated by a sliding collar *c* at the bottom of the discharge, and the material is carried over by a scraper into the mill trunnion. The method of driving is shown in the lower part of the figure.

Various forms of feed for wet tube mills are shown in the following figures—



Fig. 22. Improved Compound Mill.

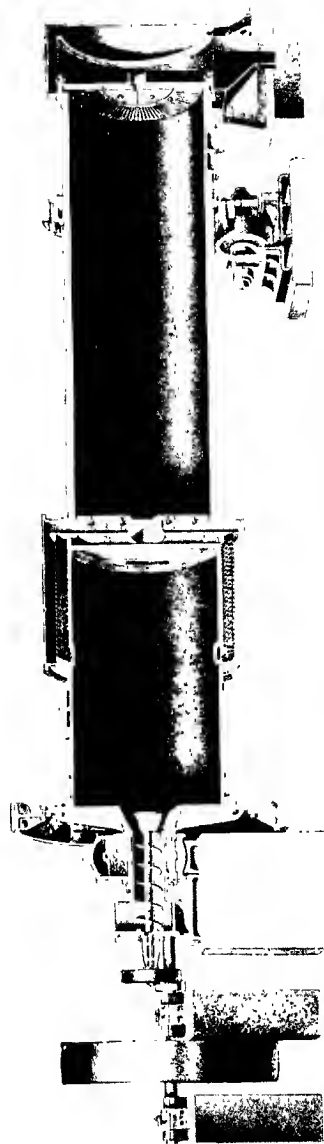


FIG. 22 Improved Compound Mill—Section I

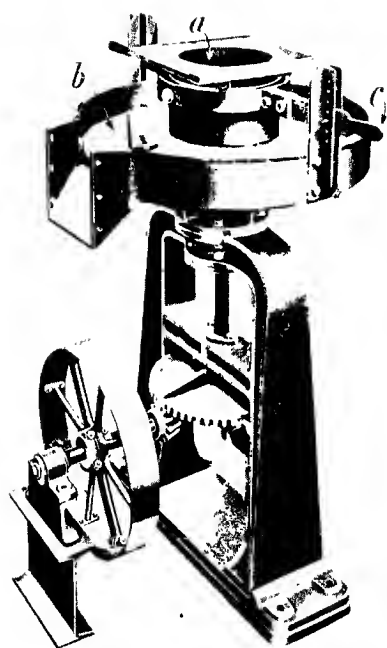


FIG. 23—Table Feed

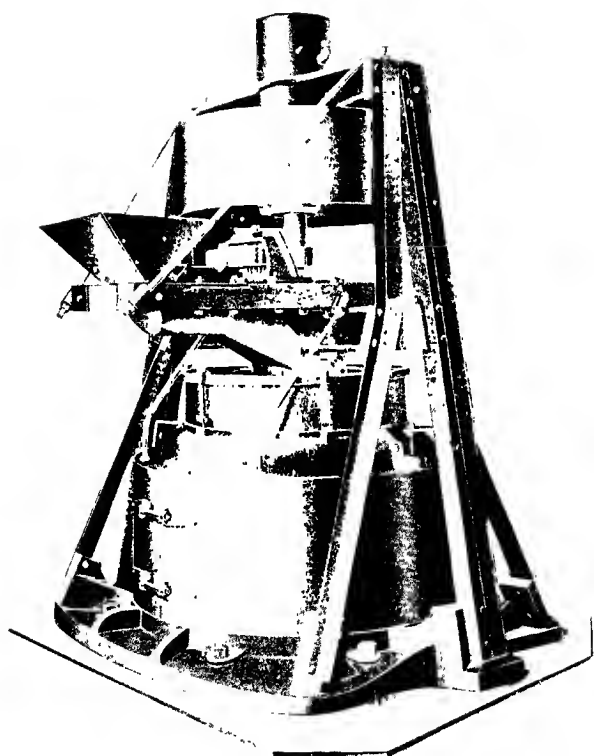


FIG. 27. Bradley Three-roll Mill.

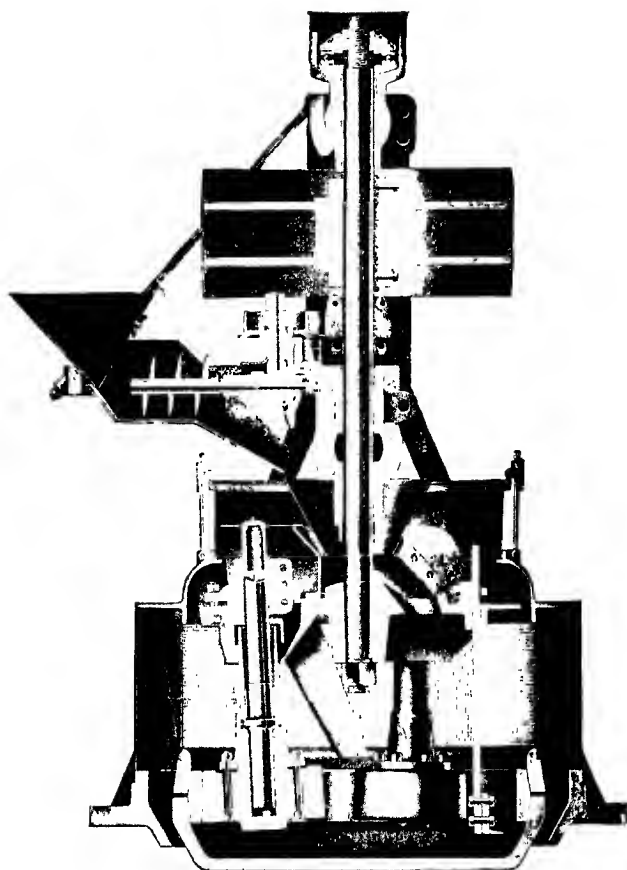


FIG. 28—Bradley Three-roll Mill (Section)

Fig. 24 shows a squirt feeder, the slurry being injected through the pipe A. The casing B with pipe C is for the purpose of catching any backward dribble from the feed.

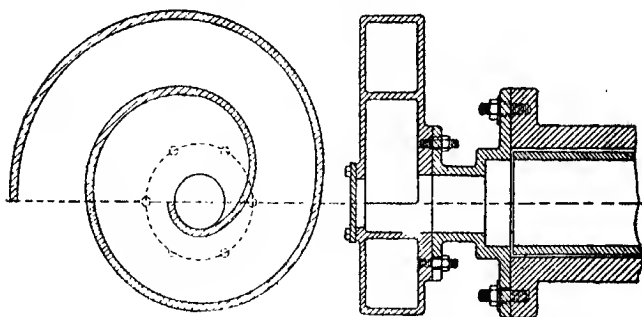


FIG. 25.

Fig. 25 shows a spiral feed and is given both in plan and section.

Fig. 26 shows an elbow feed and is fitted with a gland and stuffing-box. The feed hopper is also shown in the drawing.

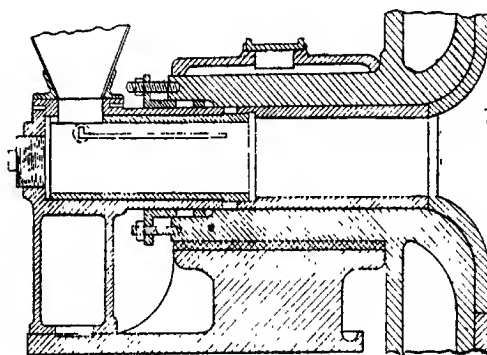


FIG. 26.

Other types of mills, suitable for dry grinding only, are given below.

Fig. 27 shows the Bradley three-roll mill, Fig. 28 giving it in section.

The principle of grinding is that of a number of rolls revolving

in and against the inner surface of an annular ring, against which the grinding is done by centrifugal action of the rolls.

The feed is arranged to deliver the material on to the grinding ring directly in front of the advancing rolls, the fine material being carried through the screen, the mesh of which regulates the fineness of the output.

The improved Giant Griffin mill is shown in Fig. 29, a sectional view being given in Fig. 30.

The grinding principle of this mill is so well known that it needs no elaborate description. It consists of a chilled iron roll revolving against a steel die ring, the roll, being securely fastened to the shaft, creating a peculiar grinding action which is very effective.

The material, crushed to three-quarters of an inch mesh, is fed in by the hopper, and the ground material passes through the screen, the mesh of which regulates the fineness of the product.

The Sturtevant "Ring-roll" mill is shown in Figs. 31 and 32.

Grinding is effected between a ring rotating in a vertical plane and three rolls which are pressed against the ring by powerful springs. An advantage claimed is that the wearing surfaces are not in contact with each other but only with the material to be ground, as that forms a layer between the two, and is held on the outer grinding ring by centrifugal force.

The Fuller Lehigh mill, of the fan discharge type, is shown in Figs. 33 and 34.

There are four steel balls which bear against a grinding ring, which naturally is concave. There is a "pusher" for each ball propelling it on its path. The grinding is in principle centrifugal, as in other mills of similar type. The ground material is drawn out by a fan *a* and thrown through a screen *b*. The particles fine enough to pass the screen are delivered to a casing *c* and thence to a shoot *d*.

It may be here remarked that in mills of this class there are both merits and defects, closely related to the mode of working. If the mill is run slowly the fan will pick up only the finest particles ("flour"), and the product will be good. If, on the other hand, the speed is too high larger particles will be picked up, and will pass the screens if they are just small enough to go through. This will give a gritty product instead of the floury one desired. The wish to obtain a large output per mill is an incentive to the latter procedure, and may lead to poor results.

Other mills of this description have been devised and put in

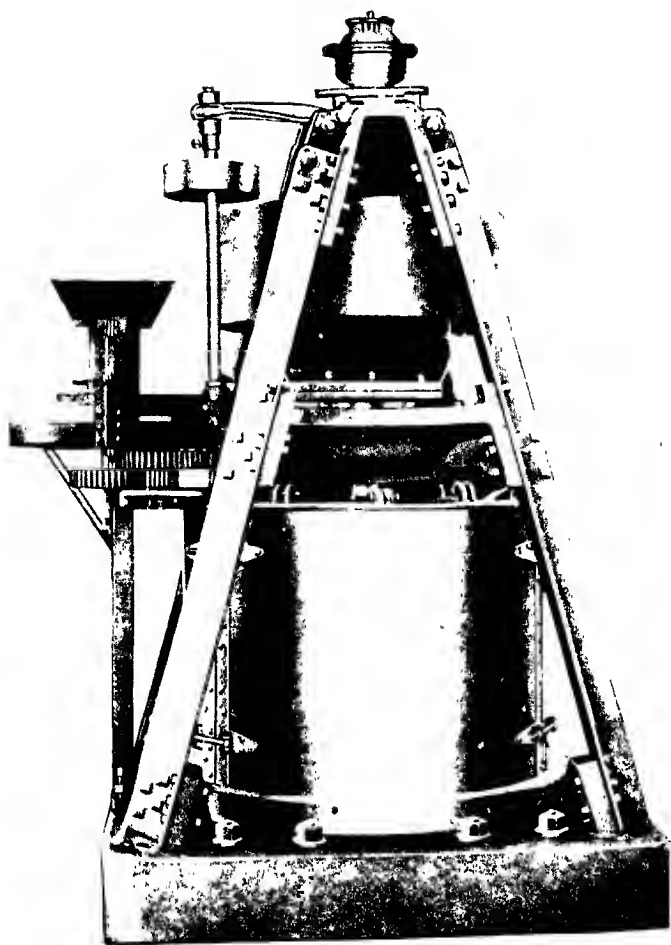


FIG. 29 - Improved Giant Griffin Mill.

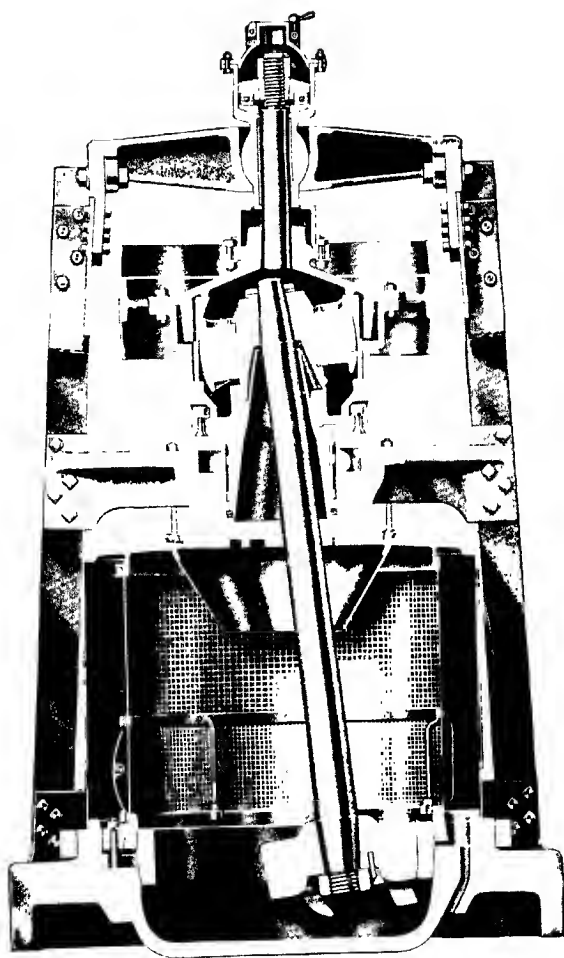


FIG. 30 - Improved Giant Griffin Mill. (Section)

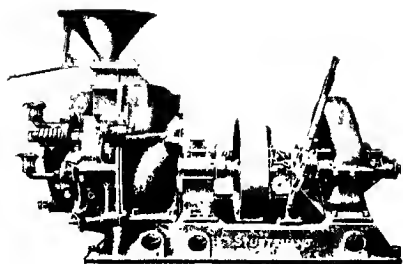


FIG. 31—Sturtevant Ring-roll Mill

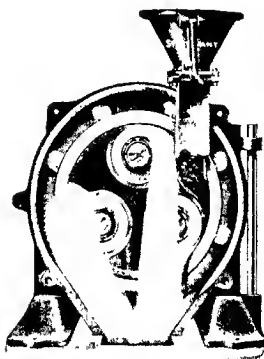


FIG. 32 Sturtevant Ring-roll Mill. (Section)

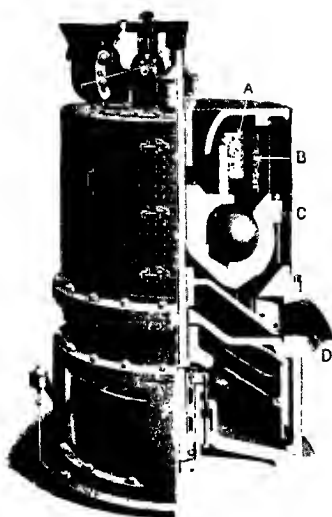


FIG. 33 - Fuller Lehigh Mill

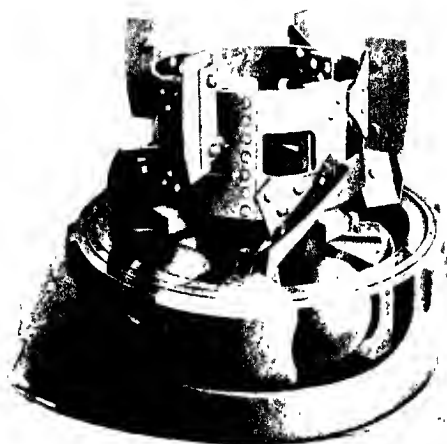


FIG. 34 - Fuller Lehigh Mill.

use, but at the present time are not in general demand, the reason being, probably, that selective action of any sort in grinding, though economical, is not necessarily the best mode of comminution. It is the *product* which is in question, and a machine like a tube mill having a large capacity and perhaps re-grinding, unnecessarily, material already sufficiently ground, may in the long run prove to be the best.

It must be fully understood that it is impossible to lay down any general principle concerning the sort of grinding plant to be preferred. The preference depends on the materials to be ground, and each case must be considered strictly on its merits. Unless this is done a plant which may be of great merit for certain raw materials may be wrongly condemned when used for others for which it is unsuitable. The best manufacturers of grinding machinery, though naturally biased by the belief in the general applicability of their plant, will acknowledge its limitations. Broadly speaking, any claim that any one type of plant is universally the best must be eyed with a wariness approaching suspicion.

DUST COLLECTING

The grinding of any dry substance, whether it be raw materials, coal or clinker, necessarily produces a good deal of dust. The dusty condition of cement works in former days was notorious and led to the prodigal consumption of beer, especially in the old-fashioned mill rooms and packing houses. The modern cement works is as free from dust as a modern flour mill. All grinding machinery is boxed and the dust delivered into flues provided with baffle plates, or into stieve rooms or some equivalent device, in which the dust is caught and returned to the process. Recently, as the recovery of potash from the flue dust from kilns has become important, various processes, relatively new, are in use. One consists in passing the flue gases, after cooling, through a series of filter bags, which are mechanically shaken and the dust collected below them. Another depends on the principle that dust can be caused to conglomerate—coagulated, as it were—by the passage of high-tension electricity.

The subject of dust collecting has become so specialised that a description in detail of the various processes and the discussion of their merits cannot be attempted in a book of this size.

As regards the collection of the dust from the dry-ground

materials themselves, the difficulty due to the high temperature of the flue gases from the kilns does not arise, and the apparatus shown in the accompanying figure (Fig. 35) is suitable.

The maker's description is as follows—

The dust-laden air is drawn by a fan into the opening in the hopper at the base, and up into the finely woven canvas tubes or bags, the air passing through the canvas while the dust remains inside. The dust-free air passes out through the duct at the top and then through the fan.

At frequent intervals and in rotation, each section of bags is automatically cut out by closing the outlet valve of that section, thus preventing the dust-laden air passing into the closed section. At the same time that section is opened to the atmosphere at the top, causing a reverse current of air downwards. The bags are then automatically shaken a number of times, as found necessary, and the dust which adheres to or lodges in the canvas bags drops or is blown into the hopper below.

DRYING

When "dry" raw materials are used, drying is desirable and often necessary. All natural rocks, such as limestone and shale, contain moisture which is not apparent in the mass, but becomes of great practical importance when the material is ground, as the finely divided material containing, it may be, only a small percentage of moisture clogs the mills and particularly clogs the screens. Hence some form of drier must be used. A good example is the Ruggles-Coles drier, shown in Fig. 36.

This consists of an inclined revolving double cylinder through which the material passes in the space between the two cylinders. The gases pass through the central space and are returned through the annular space between the cylinders and thence to the flue; the gases are drawn out by a fan. As is usual in driers the material does not go through uninterruptedly, but is lifted and allowed to drop by blades in the annular space. Heating is provided by a small furnace fed with coal or coke. At sight it would appear that the waste heat from the main thermal operation—the burning of the cement—might be used, but in practice a separate furnace is generally preferable.

An alternative form of rotatory drier is shown in Fig. 37. This consists of a double rotating cylinder fitted with blades in the annular space for keeping the material in constant contact



FIG. 35 - Dust Collector

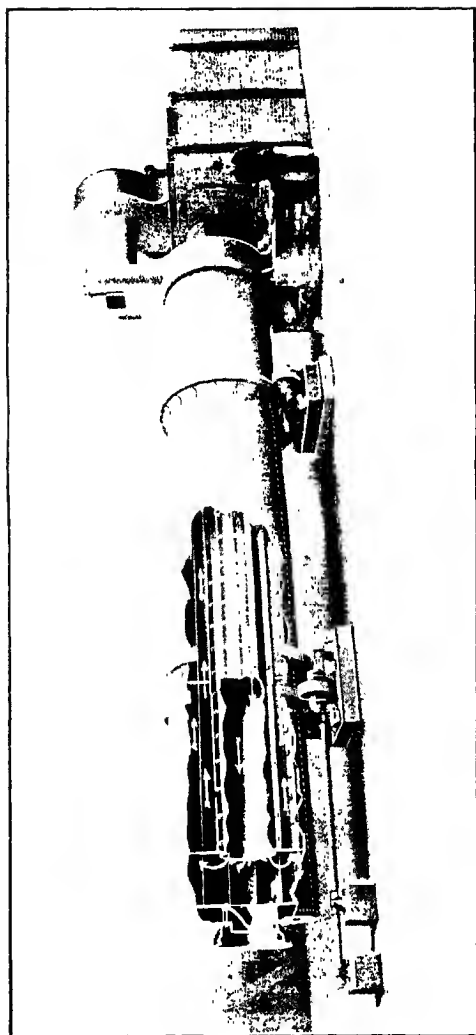


FIG. 36.—The Ruggles-Cox Diesel

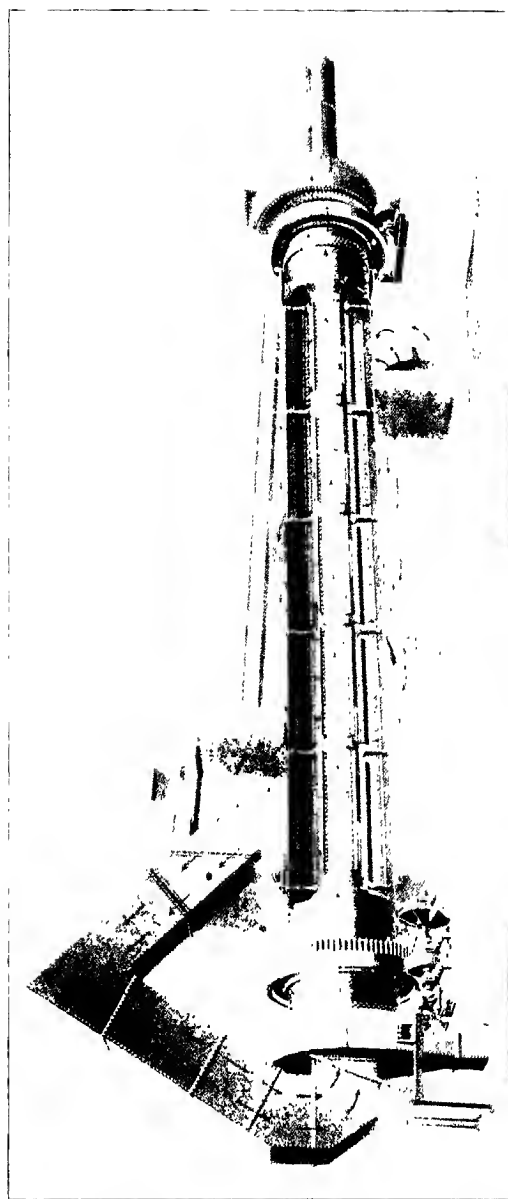


FIG. 37.—Newell's Oiler.

with the hot gases. The hot gases from an independent furnace are led into the housing of the revolving cylinder and are returned by means of a trunk through the centre of the drier to the flue. An advantage is secured by the passage of the gases over the outside of the cylinder, as loss of heat is thus diminished.

As rotatory kilns run continuously, and grinding machinery as a rule not more than twenty hours per day, it is necessary to have a good deal of storage capacity apart from the need for providing for renewals and breakdowns of the grinding plant, which are more apt to occur than with the kilns. Large ferroconcrete silos are used in modern practice. These may be circular or square in section and provided at the bottom with a hopper. The angles of repose, which will vary with the nature of the material, should be considered in the design, but more empirical methods are generally adopted, largely because the angle of repose varies not only with the nature of the material but with its dryness. The one thing necessary is that the storage capacity should be ample.

BURNING

The general development of burning has been dealt with in the earlier part of this chapter, beginning with the early and crude fixed kilns and passing to later stages, including that represented by the rotating kiln. That section is more or less historical, but may be found useful as indicating the improvement of what is, after all, the essential stage of cement manufacture—namely, the purely chemical part, where the acid and basic constituents are caused to combine. It remains to consider the present methods of burning.

A rotatory kiln consists of a cylinder made of boiler plate riveted together, or of welded steel tubes, of 100 to 250 ft. in length and 8 ft. to 10 ft. in diameter. It is lined with fire-brick, and carried on rollers so set that the kiln is inclined at a slight angle downwards to the burning zone. The ordinary inclination is about 1 in 25. The downward pressure is taken by appropriate thrust rollers. The whole structure is carried on concrete pillars and is ordinarily driven by electrical gearing. The usual speed of rotation is one or two revolutions per minute.

When rotatory kilns were comparatively novel the upper end was often unlined, but in all cases the lower end, and, in fact,

the main length of the kiln, must be lined with some refractory material. A description of the methods in use in 1898 and for a few years later is given in the Paper read before the Institution of Civil Engineers and previously referred to, from which the following extract is taken.

"The lining of the kiln is another matter which needs special mention. In order to explain the cause of the difficulties encountered when ordinary firebrick lining is used, and to indicate the nature of the remedy which has been found, a short excursion into the chemistry of refractory materials is requisite. The ordinary material used for lining furnaces is firebrick, which is substantially composed of silica and alumina; it contains, as minor constituents, oxide of iron, magnesia, and alkalis. The percentages of the chief constituents may range from 75 % of silica and 20 % of alumina, to 55 % of silica and 40 % of alumina. Such bricks behave as an acid substance towards Portland-cement clinker, which, being rich in lime, is a basic material. The acid brick and the basic clinker flux together and unite to form a fusible mass similar to blast-furnace slag. This action is inevitable at a clinkering temperature, and, if allowed to proceed, gradually causes the destruction of the firebrick lining and the deterioration of the cement clinker which is contaminated by the slag-like product of its action on the firebrick. Many attempts have been made to remove these inconveniences. As alumina acts as a weaker acid than silica, bricks relatively rich in alumina have been employed. The following analysis gives the composition of a brick of this class—

Silica	55.82
Alumina	37.98
Ferric oxide	4.02
Lime	Nil.
Magnesia	0.78
Soda	0.88
Potash	0.37
						<hr/> 99.85 <hr/>

"But this brick is still strongly acid and is severely attacked in practice. In order to prevent the clinker attacking the lining the latter must be basic. No better form of basic lining can be conceived than one composed of cement clinker itself; obviously it must be without action on cement materials clinkered in contact with it. But it is not a convenient material of which to make bricks with which the lining may be constructed *per se*.

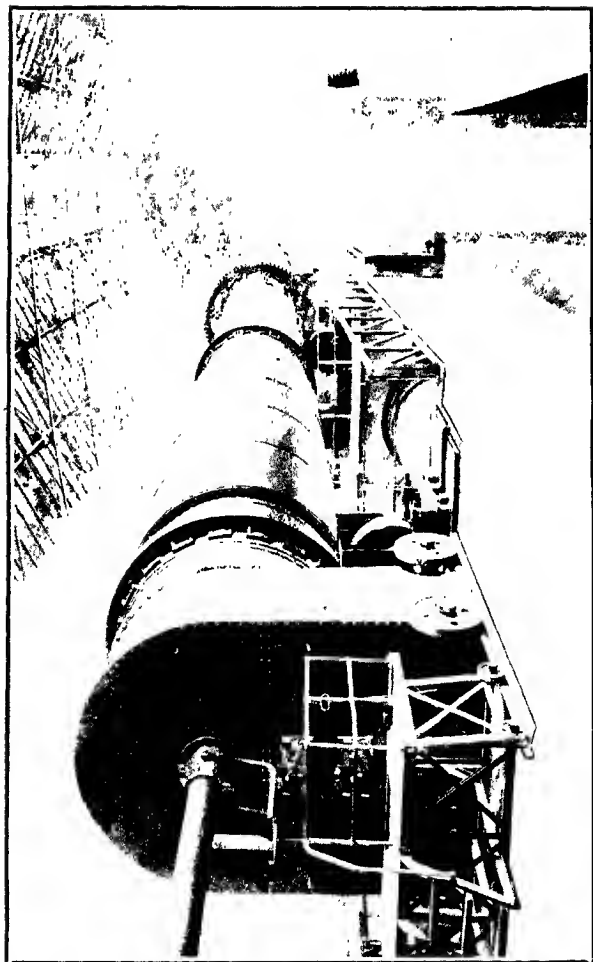


Fig. 38...Modern Rotary Kiln.

A process by which a protective coating of clinker can be applied to an existing lining of firebrick would meet the requirements of the case exactly. This process has been worked out by Messrs. Hurry & Scaman. It is executed in the following manner: A coating of common salt is applied to that part of the firebrick lining of the kiln which is exposed to a clinkering temperature. The kiln is then heated and the raw cement-material is introduced into the kiln and raised to a clinkering temperature. At this temperature it is plastic, and adheres to the heated surface, on to which it is beaten or pressed down to form an adherent protective coating. The junction between the firebrick and the coating of clinker is protected from the full clinkering temperature by the thickness of the clinker coating, and corrosion of the firebrick by the clinker is prevented. The use of salt to form a sticky surface to which the clinker adheres in the first instance, though advantageous, is not necessary; if the use of salt be dispensed with, the bare firebrick lining is heated to a high temperature, and to it is applied an adherent coating of clinker, which serves as an effectual protection of the junction of the two materials from further fluxing. This simple and beautiful device has changed the entire aspect of cement manufacture in rotatory kilns. It has abolished the whole of the difficulties which have arisen from the destruction of the lining, and has made possible the use of ordinary firebricks, which are cheap and good non-conductors of heat, in place of expensive magnesia bricks which conduct heat too freely and are, moreover, liable to crack."

Later experience has modified this practice a good deal. It is no longer sought to obtain firebrick of especially "neutral" quality, nor are special efforts made to provide a basic lining to protect the firebrick from the clinker. There is always some attack and some adhesion of the clinker to the firebrick, but with proper regulation of temperature the attack is not so intense as to destroy the lining rapidly. Of course stoppages for occasional repairs are necessary, but it may be said that whereas in earlier days the lining question was regarded—and rightly regarded—as of great importance, it is now looked upon as a secondary matter, much as the inevitable replacement of boiler tubes is regarded.

The accompanying Fig. 38 shows a modern kiln of Messrs. Smidth of Copenhagen 230 ft. long and 10 ft. in diameter. It has an enlarged burning zone having a diameter of 11 ft. 4 in.

This is claimed as an advantage by some makers, while others prefer a cylinder of equal diameter throughout. The larger burning zone allows of longer "soaking" of the clinker at the burning temperature, and this is certainly a merit. On the other hand, the construction of a cylinder of uniform diameter is simpler. It will be seen in the figure that there is a large housing or hood at the burning end through which passes a pipe carrying the fuel—powdered coal. The kiln is driven at about the middle of its length by spur gearing. In the illustration the position of a second kiln is shown, to be afterwards installed. This is general practice, as it is economical to build the sheds and other permanent structures so as to allow of duplication of the plant when required. Below the kiln is seen the cooler, which is shown more clearly in Fig. 39. It consists of a rotating cylinder into which the red-hot clinker drops. This part of the plant varies a good deal in different makes, but in the present case the clinker makes two journeys through the cooler, meeting air driven in by a fan, the air passing to the kiln. The clinker finally passes into the hood shown in the figure and falls through a hopper into trucks.

It will be understood that there are other forms of cooler, some of which consist simply of a rotating cylinder like a small kiln and having a current of air passing through them and then to the kiln. In many cases water is sprayed on to the hot clinker for a final cooling, and incidentally to slake any "free lime" which may remain from imperfect mixing or burning. The same purpose is sometimes served by storing large masses of clinker, slightly moist on the surface, and allowing slow slaking to proceed. Such practices, though sometimes necessary, are a tacit confession that the clinker has not attained that state of perfection at which the cement-makers aim. There is, however, a good deal to be said for them, as they afford a safeguard to the consumer against that most dangerous of materials, unsound cement.

Taking this sketch as sufficient to give a general idea of a modern rotatory kiln, the course of the raw material may be followed from the time it leaves the grinding plant to its exit from the kiln as clinker. In the case of wet raw materials, these, when finely ground and of correct composition, are pumped to the upper end of the kiln by a pump, usually of the type shown in the figure (Fig. 40). It is of simple design and consists of three cylinders with single acting plungers driven by a three-throw



FIG. 30 Modern Clinker Cooler.

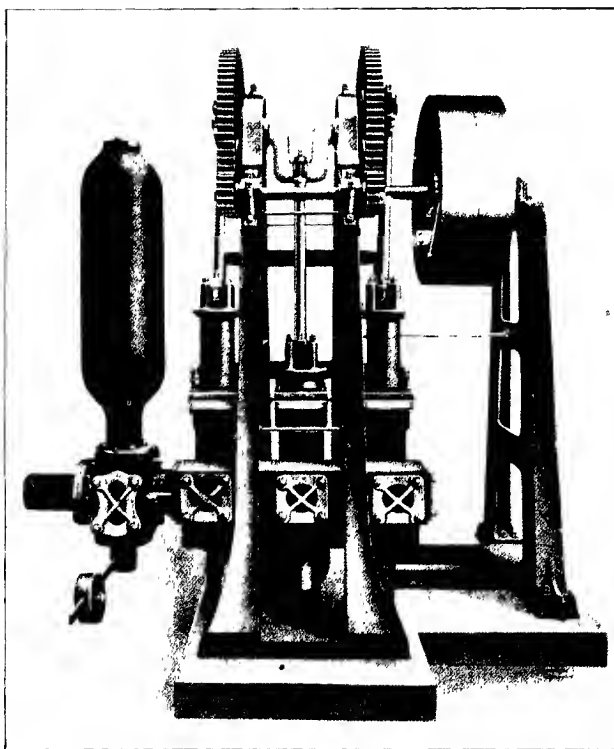


FIG. 40 - -Newell's Slurry Pump.

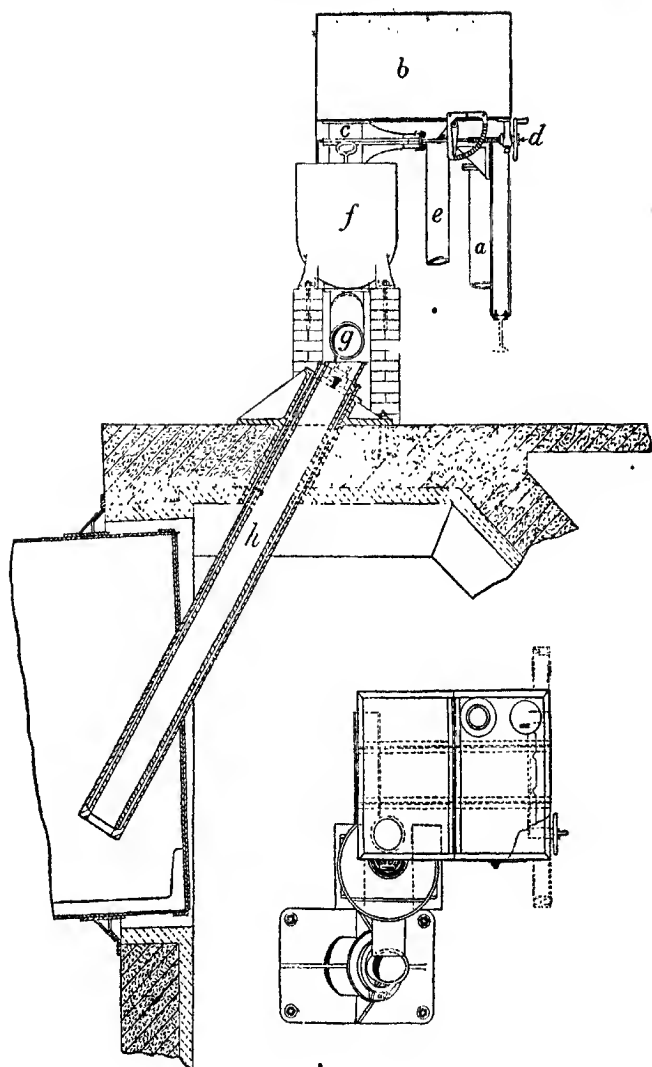


FIG. 41.—Kiln Feed.

crank. There is an air chamber to take up shock, and a relief valve to allow the slurry to escape should a stoppage in the system occur. The pumps are designed to deliver more than the maximum consumption of slurry into a feeding trough, the surplus being returned to the tank from which the pumps draw. The details of one such arrangement are shown in the accompanying figure (Fig. 41). The slurry is delivered by the pumps into a storage tank *b* provided with an outlet valve *c*, with a hand control *d*, and an overflow pipe for the excess *e*. From this storage tank the slurry flows into a receiver *f*, which is

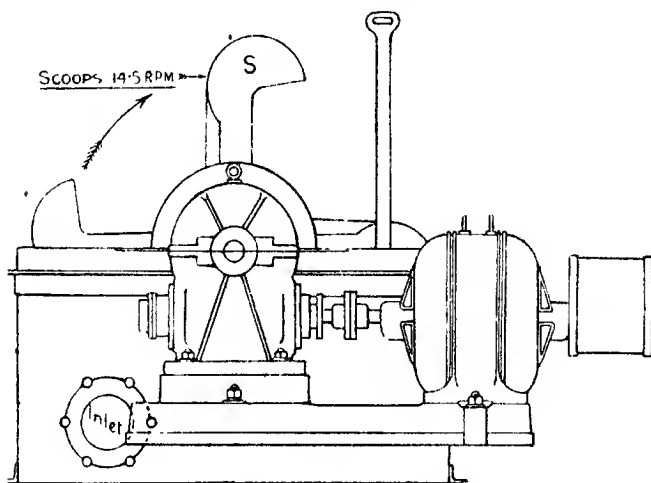


FIG. 42.—Kiln Feed. (Spoon type)

provided with a weir so as to maintain a constant head. From this receiver the delivery pipe *g* carries the slurry to the feed pipe *h* and then to the kiln.

Another type of slurry feed is the scoop feed, which is shown in Fig. 42. This consists of a slowly rotating wheel, provided with scoops marked *S* which deliver the slurry into the compartment from which it gravitates to the kiln feed pipe. In this case there is no necessity for a return, as the feed is positive.

In the case of dry raw materials the use of a dosage tank employed for slurry is obviously, inapplicable, and the equivalent process of adding a little of either dry raw material before it passes to the kiln, though possible, is troublesome, and rarely

used. It follows that extra care must be taken to provide precisely the right proportions from the outset. And here it is proper to remark that the complete dryness of the raw materials is essential, as in their natural condition the content of moisture varies, and although that is easily determined the materials have passed into the kiln before correction can be made. Assuming that the materials are dry, they are automatically weighed according to their composition and conveyed to the grinding plant. From the grinding plant the finely-ground material is taken by conveyors to hoppers of sufficient capacity to allow of regular feed to the kilns, not only in ordinary work but during accidental stoppages of the grinding plant and over week ends, when as a rule the plant is at rest though the kilns run on.

The usual practice is to pass the mixed dry meal to the kilns by worm conveyors with variable rate of feed. Sometimes the dry meal is damped just before it enters the kilns in order that there may not be too much dust going into the flue. On the whole, it may be said that this is a makeshift, and that it is better to face the dust difficulty by catching the dust with baffle plates and the like, and this has been spoken of.

The foregoing general description will give an idea of a typical plant of this date, but it may be of interest to record the development of the modern rotatory kiln. Enough has already been said in a previous chapter concerning earlier attempts and their outcome, but the following will serve to give an idea of the evolution of the modern plant. Fig. 43 shows a set of kilns each 60 ft. long and 6 ft. in diameter. The clinker dropped into a hopper and thence into a truck. The fuel feed was by an injector, the coal dust being fed from a hopper much as in present practice. It will be observed that the feed of slurry was much as at present, and that considerable precautions were taken for storage of the slurry and incidentally its blending, so that the mixture fed to the kilns was fairly uniform. The old saying, "cement is made in the wash mill," holds here as much as it did in the days before rotatory kilns were dreamed of. It will be noted that the driving arrangements are rather primitive, the whole set of kilns being driven mechanically off a main shaft. Nowadays distributed electrical driving is general. The gradual growth of the size of kilns is interesting, those illustrated being less than a third the length of the modern kiln and of vastly less capacity and output, but the principle remains unaltered.

Another good example of what may be regarded as an intermediate stage of development is shown in Fig. 44. This shows a kiln working on the wet process, the feed being of the overflow type. The burner is driven by a fan and is in a removable hood. The coal passes through a rough crusher, is elevated to a hopper over the drying drum through which it passes to the elevator to the ball mill, where it is ground; then to the tube mill, and so to the feed hopper. The dry and finely powdered coal is driven by a fan through a pipe in the hood into the kiln. The clinker falls into a shoot and then into a rotatory cooler. From the end of the cooler it falls on to a shaking conveyor and thence to the grinding plant.

A sufficient description has been given of the kilns themselves, both in regard to their origin and development, but certain details of construction and use may be considered. As already mentioned, general practice is to construct kilns of boiler plate riveted together, but in some cases they are made of steel tubes welded longitudinally and riveted together length to length. In earlier days the upper part of the kiln was left bare and sometimes provided with blades intended to stir the slurry as it flowed down the kiln. This has been abandoned in the latest examples, and the kilns are lined throughout with fire-brick. It seems unnecessary to line a kiln at a part where the temperature is low, but a little reflection will show that simplicity may be preferable even if it involves a small expense. As the lower end of the kiln *must* be lined, it is better to make a circular arch of fire-brick from one end to the other without a break, such as would be caused by a change from brick to bare steel.

The preparation of the coal for burning is of equal importance. The composition has been dealt with in an earlier chapter, and the method of drying usually employed has also been described. As small coal is used, only a slight preliminary crushing is necessary, and this is done by rolls, bringing it down to about one inch size. At this stage it goes through the dryer, and then grinding properly begins. The grinding is usually carried out either in mills of the centrifugal class, such as the Griffin or Fuller mill, or in ball and tube mills. Both types have been described above. The dried coal, ground to pass 100-mesh sieve, is stored in hoppers and fed to the kilns by various methods. Two may be cited. In both the powdered coal is mechanically driven towards the kiln by screws and then is propelled by a blast of

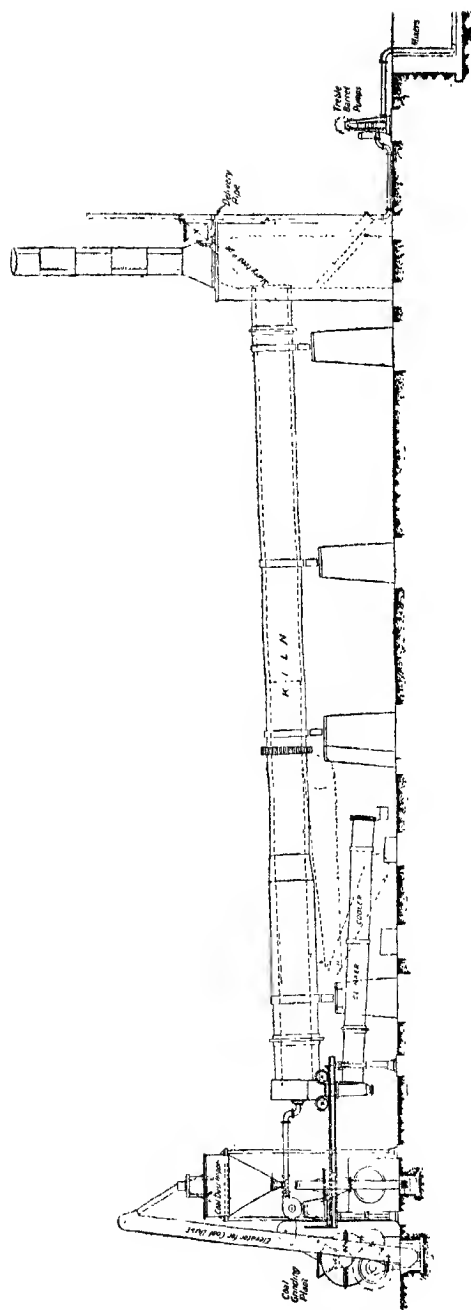


FIG. 44.—Rotatory Kiln. (Intermediate type.)

air. In the older form, notably that of the pioneer plant of Hurry & Seaman, the air was provided by a compressor, and this method has been largely used. In the Hurry & Seaman plant elaborate arrangements were made to allow of the ingress of secondary air before final combustion took place in the kiln. Although most ingenious and theoretically excellent, yet the process and apparatus were costly, particularly as a compressor is a wasteful machine for propelling air, and should only be employed when necessity compels. Simplicity prevailed, and propulsion by a fan at low pressure has practically superseded the compressor process.

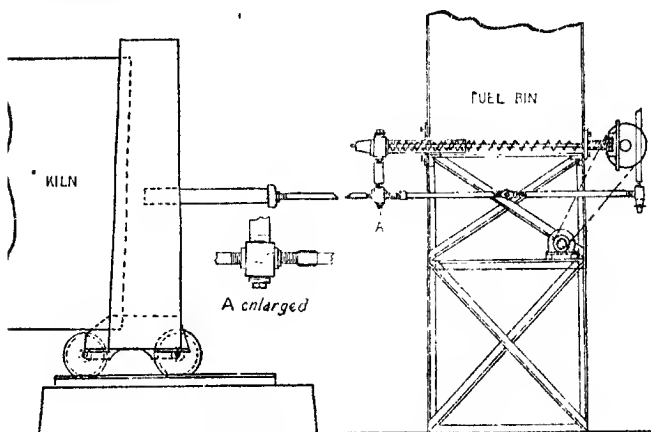


FIG. 45.—Coal Feed. (Injector type.)

Both systems are shown in the drawings. The first (Fig. 45) shows the coal driven by a screw into a pipe into which is injected a blast of air at high pressure: the nozzle of the injector is shown at A.

The second (Fig. 46) is the later form working with a fan at low pressure. The drawing given shows the arrangement. A is the hopper containing coal dust, B is a twin screw extractor removing the coal dust to the pipe C, where it meets the blast from the fan. The feed is controlled by the variable speed gear D, and the coal is delivered into the kiln through the nozzle E. It will be seen that the arrangement is of a simple and practical nature. The reason for the earlier and more elaborate devices was that it was believed that something like

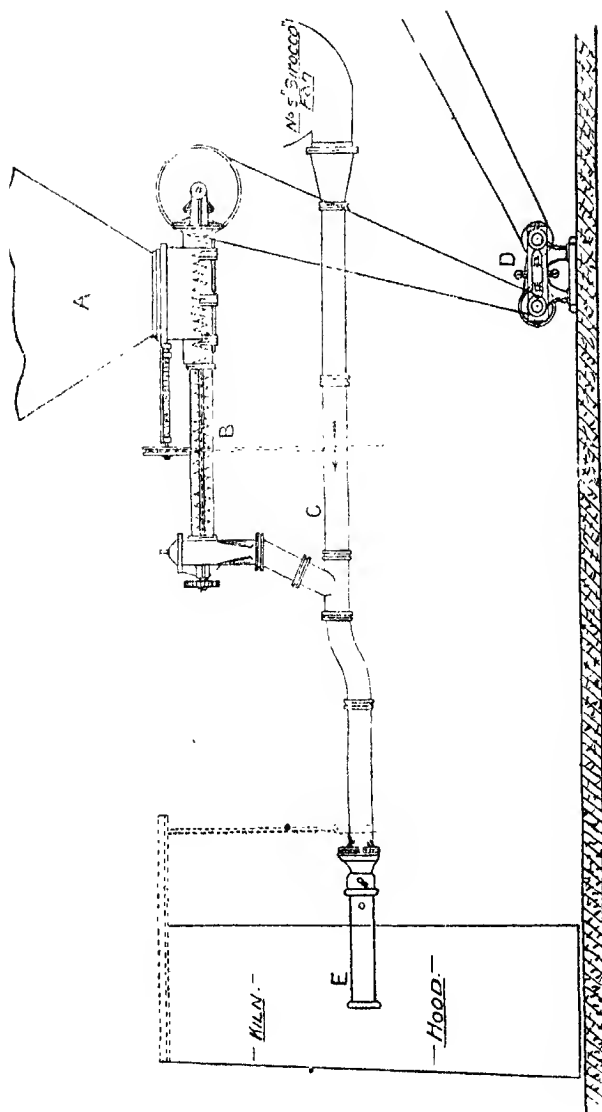


FIG. 46.—Coal Feed.

a blowpipe flame with air and fuel nicely adjusted was necessary. This proved to be an error because, provided the coal is finely divided and hurled into the kiln, it matters very little how it is hurled. It might be hurled by nitrogen. The real combustion is in the kiln itself.

The whole of the kiln system is under the control of the burner, who may be in charge of two kilns, or of three if he has an assistant. It is skilled work but not difficult, as the temperature on the burning platform is not excessive, and the control nowadays is easy with kilns provided with variable speed gear electrically driven. One discomfort is the glare from the kiln when the door is opened, but blue glasses provide for this. The writer when examining the working of a kiln never uses these, preferring to allow his eyes to become accustomed to the glare, and then seeing the condition of the burning zone more accurately. But this is quite impracticable for a man working on the platform for many hours a day, and day after day, and good optical protection is absolutely necessary.

The clinker as it comes from the kiln should be perfect in composition and soundness, but this is rare. Often it is quenched by a stream of water directed either on to the clinker as it drops from the kiln or from the cooler. Sometimes it is stored in large dumps protected from direct rain, but open to the weather. The condition of the clinker in such dumps after storage is a fair indication of the degree of imperfection in the manufacture. Large whitish nodules looking much like slaked lime may be regarded as an index of bad mixing, bad burning, or both. The practice of storing in dumps, though not ideal, has a certain advantage. In the first place there is afforded an opportunity for under-burnt material to hydrate and become innocuous. Also there is a reservoir of stuff on which the manufacturer can draw according to the requirements of his trade. But it must be remembered that all this means double handling and is economically bad. A works running under perfect conditions will deliver cement ground from faultless clinker straight into casks or bags, reserving in store only so much as will provide for fluctuation of demand.

The grinding of the clinker is conducted in mills of the type already described. In the case of tube mills steam is sometimes injected with the view of hydrating any under-burnt particles.

It has been found that the setting of cement differs considerably according to its method of manufacture. In the old days when fixed kilns alone existed, quick and slow setting cements

could be manufactured by varying the composition of the raw materials.

Thus, broadly speaking, the lower the lime content and the higher that of alumina the quicker the cement sets. Also if the setting time was inconveniently short, it could be prolonged by aeration of the cement by storage.

These questions, though not even now fully understood, are dealt with according to current knowledge in a later chapter. Putting aside the cause for the moment, the fact remains that the setting time of fixed kiln cement could be controlled without much difficulty. When rotatory kilns superseded the older types, troubles as regards setting time arose at once. It was found that on account of the higher temperature a large part of the sulphuric anhydride naturally present in the raw materials did not appear in the clinker but went up the flue. The obvious remedy was to add sulphuric anhydride in some form or other to the cement as it was being ground. Either raw gypsum or plaster of Paris from broken casts was usually employed, but it was soon discovered that the retarding effect of these materials is evanescent. Again, the chemistry is obscure, though the fact remains.

Further, it appeared that rotatory clinker often had a "flash set"—that is, it set almost immediately when freshly ground, and shortly afterwards set too slowly to be conveniently used in the work. Control of these variations is usually accomplished by the use of plaster of Paris, but there is still the difficulty that the effect of the addition of sulphates is neither uniform nor permanent.

To consolidate the reader's ideas it may be useful to print a description of typical works. The first is an excellent example of a modern works built by Messrs. Smidth on the site of an old works with fixed kilns. The raw materials are those usual in the district, consisting of chalk and clay of the usual good quality used at Thames and Medway works. A description of the works, taken from *The Times Engineering Supplement*, is appended. The writer knows the works and accepts the description as correct.

"It is a matter of common knowledge that the Portland-cement industry in this country has been passing through seasons of great vicissitude, and that during the past few years it has become necessary for much of the old plant to be consigned to

the scrap-heap. It is scarcely too much to say that in the short space of a decade the whole process of manufacture has been revolutionised, and that many works thought to be efficient and up-to-date at the close of last century have been proved to be completely obsolete and incapable of being conducted at a profit.

"A change of this character has taken place at West Thurrock in the works of the Tunnel Cement Company, originally erected in 1874, which have now been reconstructed and equipped with entirely new plant by Messrs. F. L. Smidth and Co., of Copenhagen. The original works, kilns and all, have disappeared and the only trace of the old buildings is a part of the former warehouse. The works may be now looked upon as being typical

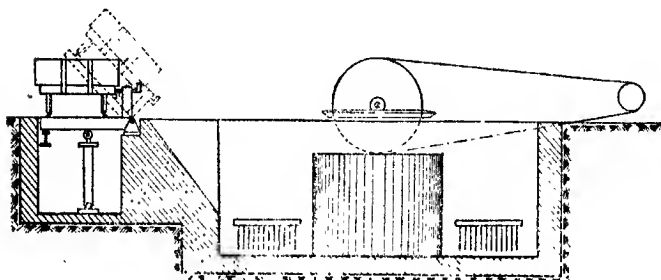


FIG. 47.—Wash Mill. (Tunnel Works.)

of the modern methods introduced into this branch of manufacture. The most remarkable feature is the great length of the rotary kiln and the extreme uniformity of the quality of the cement, consequent upon the employment of single units of the largest size.

WASH MILL

"The chalk, brought in trucks from a neighbouring quarry, and the clay, also loaded in trucks, are conveyed to the edge of the wash mill, and after being weighed are tipped by hydraulic pressure, in truckloads at a time, into the wash mill (shown in Fig. 47), capable of dealing with 50 tons of raw material an hour. The chalk and clay are reduced to slip or "slurry" by revolving stirrers of the drag-harrow type, and the slip is pumped up to the separators, where the coarse particles are removed. This is effected by centrifugal wringers, the sides of which are lined

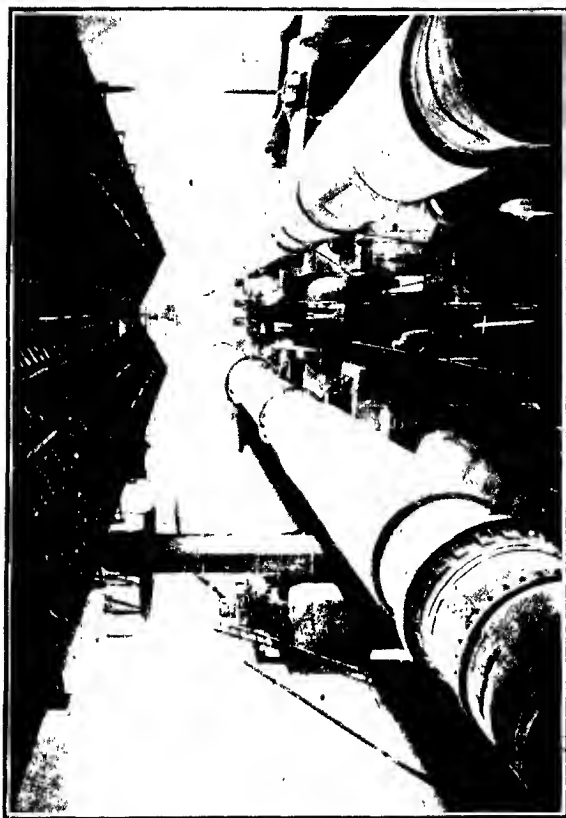


Fig. 4. Kals - Tunnel Works

with wire gauze that permits the fine particles in suspension to pass through, but retains the coarser matters for return to the wash mill. The roughly screened slurry, after being further ground in a tube mill, is run into a series of tanks, provided with stirrers in order to prevent deposition, after which it is lifted by a pump to the top of the kiln building. This is a fine hall, about 240 ft. in length by 55 ft. in width, containing two rotary kilns with clinker-cooling cylinders and coal-grinding plant. A photograph is given (Fig. 48).

ROTARY KILN

" Each rotary kiln, into the upper end of which the slurry is introduced at the rate of about 45 gallons a minute, is inclined at an angle of 1 in 25 with the horizontal and is supported on five sets of friction rollers. Each kiln, which is 210 ft. in length by 8 ft. in diameter, increased to 9 ft. near the firing end, is driven by powerful gearing at the centre and revolves at the rate of one complete turn in 65 sec. It consists of a tube, formed of mild steel plates riveted together, and lined throughout with firebrick. The fuel, which is Newcastle coal ground to a fine powder (about 15 % residuum on the 180-mesh sieve), is blown into the kiln by a high-pressure fan, and the air needed for combustion, previously heated by being passed over the red-hot clinker quitting the kiln, is also blown in by a fan. This kiln, when in normal work, is capable of yielding $7\frac{1}{2}$ tons of clinker an hour, with a fuel consumption equal to 28 % of the weight of the cement. The coal is ground in a 'kominor,' or ball mill, and is finished in a tube mill, whence it is raised into a feeding hopper.

GRINDING PLANT

" The clinker, as it issues from the cooling cylinder, placed beneath the rotary kiln, is lifted by a conveyor into a storage-hopper, whence it is removed in iron trucks and wheeled by hand on a narrow-gauge railway to the mill house. The kominator into which it is tipped along with a measured quantity of gypsum, to delay the setting time of the cement, will turn out 10 tons of finely crushed clinker an hour, and the ground material from the kominator is conveyed to the tube mill, 6 ft. 6 in. in diameter and 24 ft. in length, in which the cement is ground to an extremely fine powder. The specified fineness of grinding is 12 % residue

on the 180-mesh sieve. The ground cement issuing from the tube mill is transferred by a spiral screw conveyor to an endless rubber belt, 170 ft. in length, leading to the silos, six in number, 30 ft. in diameter and 50 ft. in height, with a united capacity of 10,000 tons of cement.

AUTOMATIC SACK FILLING (Fig. 49)

"The use of the 'Exilor' machines for sack filling constitutes a marked improvement on the old-fashioned plan of working. The empty sack, attached by clips to the orifice of a tube leading from the silo, is shut into an airtight chamber, formed in two sections, and in the act of closing the door an air-exhaust is started. Owing to the vacuum created a stream of cement from the silo is drawn through the tube into the sack. The sack is hung at one extremity of the beam of a weighing machine, in the scale-pan of which is the exact weight of a filled sack. In 10 or 12 seconds the requisite quantity of cement has been drawn into the sack, which then tilts the beam, thereby opening the air-valve: this breaks the vacuum and stops the flow of cement. The opening of the door to remove the sack enables a small fan to carry away the dust from the mouth of the sack and the door is ready to be swung back and closed against the other chamber of the Exilor, in which another sack has in the meantime been fixed in readiness for filling. The door is hinged on the centre line, so as to be capable of being closed against each section of the chamber in turn. A gang of three expert workmen fill and wheel away 120 sacks of cement in the hour, with the precise weight required in every sack. A small air pump, driven by motor, is all the power needed to convey the cement from the silo into the sack, and the vacuum created is about 15 in. of mercury.

POWER HOUSE

"The power throughout the works is generated electrically and is conveyed by cables to the various machines. The power-house is a handsome building, containing ample space for additional plant. At present a steam turbine driving a powerful dynamo, furnishing three-phase current at 50 periods per second, is the main source of supply, but there is a 250 h.p. gas-engine to serve as a stand-by. The total weight of the turbine and dynamo is 27 tons, whereas the fly-wheel alone of

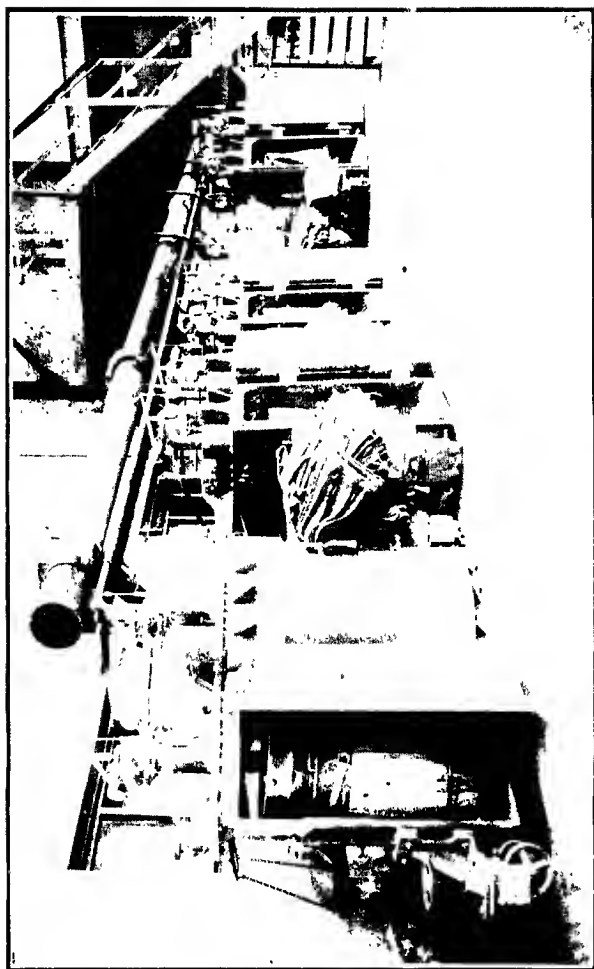


Fig. 49. "Premiato Packer".

a reciprocating engine to furnish the same amount of power was estimated to weigh over 50 tons. Steam is supplied by two Steinmüller boilers, each of 1000 h.p., with chain grate stokers."

The following description of a plant for dry raw materials may be taken as typical, and for clearness a plant actually running is chosen, but it must be understood that modifications would be necessary in some cases, the instance given being regarded as an example only.

The raw materials are a hard limestone and a shale. The limestone is crushed at the quarry and the larger pieces are sent to chemical works. The smalls are shipped to the cement works. The crushers are ordinary jaw crushers and the material is sized by rotatory screens similar to those used for sorting road metal. The smalls are about one inch in their largest dimension. The limestone rock is substantially dry. The shale is quarried from the hillside and taken by trucks to the crushers and screens, and then by a travelling band to large hoppers on a railway siding. From these it drops into trucks and is sent to the cement works. As the material is a shale its condition as regards moisture varies appreciably, and, moreover, will be altered in the course of its journey according to the weather.

The limestone coming by water is stored in bins at the wharf and thence dropped into trucks which are hauled to the cement works a short distance away. The shale is delivered by rail direct to the works. Both are shot into storage bins and dried in rotatory driers of the Ruggles-Cole type. These driers have already been described. From these the dry materials, still about one inch cubes, are elevated to hoppers over weighing machines, where their proportions are adjusted. The material from the weighing machines is dumped into a hopper, and thence fed to a revolving cylinder, where it is roughly mixed. It is still unground. The function of the cylinder is merely to make an approximate blending of the two materials. The materials are then discharged into the boot of an elevator, which lifts it to the top of the building and discharges it on to a belt conveyor, which delivers the mixed material to the mill hoppers. From there it is released to the mills, which may be ball and tube, Griffin or Fuller, all of which have been described. As perfect admixture is not so easy with dry raw materials as with wet ground to a slurry, the ball and tube equipment has advantages, as the tube mill has a considerable capacity, and small errors of

proportion adjust themselves there. The mills deliver into a common conveyor, and the material is elevated to the main storage hopper, whence it is distributed to the kiln hoppers. The material is extracted by a screw conveyor and fed to the kiln. In some works it is damped as it goes in to prevent the dust, which would otherwise be carried by the draft of the kiln into the stack. The kilns are of the same build as those used in the wet process and have already been described. The remaining stages of the process are identical with those already mentioned, and the product is handled in the same way. The preparation and injection of fuel is also the same. The essential difference of the two processes is that in the case of the dry process it is as necessary to have the raw materials thoroughly dry as it is in the wet process to have them thoroughly wet, and that there is certainly more difficulty in making a homogeneous mixture of dry limestone and shale than there is of chalk and clay. But the difficulty is easily met by exact working, and the working of dry materials by the wet process, though possessing merits from this point of view of intimate admixture, does not commend itself thermally.

In one case the clinker is taken from pits below the kilns on a conveyor, elevated and distributed in dumps. The same conveyor receives the stored clinker and carries it to a cross belt, which conveys it to the mill hoppers. From the mills it is conveyed to the storage bins and thence to the automatic packing machines. It will be seen that in modern practice as little man-handling as possible is done—a great contrast to older methods. But there is an economic limit in this matter. The wear and tear of belts and conveyors, and their frequent breakdown because they handle such a dusty and gritty material as cement, must be set off against the cost of manual labour, and it is sometimes a nice point to decide when mechanical methods should stop and barrow-pushing begin. The writer is familiar with works of both types where the supposed advantage of one plan or the other has been driven unreasonably far. In short, the local conditions *must* be considered by some one not wedded to a system, however good in itself.

PACKING

As regards packing, the "Exilor" system described below and shown in Fig. 49 is an application of a device designed by

the author some years ago for sampling cement in the heap. A description of the sampler is given in the chapter on analysis and testing. The commercial application of this principle is common in such machines as grain elevators, but as far as the writer knows it has been adopted for cement only by Messrs. Smidth, whose description is here transcribed.

“ The container, whether this is a sack or a barrel of any form or shape, is placed in an airtight chamber connected by means of a pipe with the material to be packed and with an air pump. By means of the latter a vacuum is created in the airtight chamber, and the material will flow through the pipe, the mouth of which must be placed in a position so that the material falls into the container.

“ To bring this principle into a practical form the airtight chamber is provided with a door, through which empty containers can be put into position, and filled ones taken out.

“ To utilise the apparatus fully the time which would otherwise be wasted by placing the empty containers and taking the filled ones out is utilised by making the apparatus double-acting, having two separate vacuum chambers, one man being able to look after both.

“ The Exilor for pneumatic packing is at the same time an automatic weigher. This is done by hanging the container up on one end of a beam, at the other end of which weights can be placed to govern the exact weight of material required in each package, and arranging a simple system of valves, by which the connection with the air pump is broken off the moment that the correct weight is filled into the container, at the same time forming a connection with the open air.

“ The Exilor for pneumatic packing works absolutely dust free. The process of filling the container takes place inside the closed chamber, and in the vacuum the dust particles will fall straight and solidly down into this. The moment that the outside air is admitted there will certainly be a sudden development of dust, but the Exilor is provided with a small fan, which automatically clears this dust away from the back of the chamber and disposes of it either into a dust filter or else into a permanent dust collecting pipe serving all the machines.

“ The Exilor for pneumatic packing is a portable apparatus, which without any difficulty can be moved from one place to another, and by a flexible tube can be connected up with the

suction pipes inserted at the bottom of the various bins or silos."

It is of great importance to have on the works a chemist of knowledge and experience who can control the quality of the raw materials and the finished product. His duties consist in analysing the raw materials, the mix, the clinker, the coal used for burning it, and for power purposes, the flue gases and any auxiliary substances such as gypsum, which may be used for regulating the setting time. In addition he must be able to carry out the usual mechanical tests as regards tensile and compressive strength, setting time and the like. As a large works running night and day has hundreds of samples per week to be analysed and tested, it is quite impracticable for this work to be done without an adequate staff, and the chief chemist should be relieved of the necessity of carrying out routine work himself. But he should know it through and through and be able to execute any of the usual operations himself, either at a pinch or to educate a new assistant. In short, he must have been through the mill himself.

The usual methods of analysis and testing are more conveniently described in sections by themselves.

CHAPTER V

POWER

THE question of power for a cement works is secondary only to that of raw materials. Evidently a fairly cheap supply of both is necessary for a successful undertaking. It is assumed, of course, that the supply of both raw materials and power is not made impracticable by cost of transmission. The word transmission is advisedly used, as it includes freight of every sort, whether mechanical or by the direct utilisation of electricity.

In general the primary source of power for cement works is coal, but wherever petroleum is available it may be used with advantage. Apart from cost, petroleum must be preferred, as it needs no preparation and can be used for all purposes just as easily as gas can be by turning on a jet, and is as easily regulated.

The coal may be used in various ways. The ordinary plan is to burn it under a boiler, carrying in the coal mechanically or shovelling it in by hand.

But seeing that burning on a larger scale than that of ordinary steam-raising in a cement works can be done by injection of powdered coal, just as in the case of a kiln, there appears no reason why the same method could not be applied to boilers. It may be urged that this method of steam-raising is unconventional, and that that view must be accepted and then its consequence discarded. It must be remembered that boilers which are the most heavily pressed—that is to say, naval boilers heated by oil fuel—work with complete success, and as powdered coal is merely equivalent to liquid fuel, injected in much the same way as oil fuel is injected into the furnace of a naval boiler, there appears no difficulty in adopting pulverised coal as a means of obtaining power for a cement works. Those objections of any weight which have been urged relate to one or both of two things: these are the difficulty of burning powdered coal in order to heat a boiler of the conventional type, and, supposing that were done, the difficulty of collection of ash from the burning coal. Both

these objections may be put aside at once. It will certainly be necessary to burn the jet of powdered coal in a large fire-box, and it is also certain that, with the blast behind it, a great part of the ash of the powdered coal will be carried through the flues of the boilers, but it is equally certain that neither of these things presents any mechanical difficulty.

Now, when it is considered that the total consumption of fuel in a cement works turning out 50,000 tons a year is 25,000 tons a year, and that of this quantity about three-fifths is used for the actual burning of the cement, for which purpose it must be reduced to a fine powder, it follows naturally that the balance were better used for raising steam if steam is the prime mover.

This is only one side of the essential question of the provision of power in cement works, the total amount of which may be taken as about 30 % of the total working cost. It must be understood that these figures relate to normal prices of fuel and not to war conditions.

There are other methods of obtaining power. I do not think that any one at present has been bold enough to take his total amount of power from a public supply, because that is usually too dear, but there are certain districts where coal is cheap and local power plants are large, which might well supply a good-sized cement works at a reasonable rate.

I would instance the Potteries, where power can be obtained at about a halfpenny per Board of Trade Unit. There comes in the question of material; there is plenty of clay in the pottery district, but it is already utilised for its proper purpose, and as far as I know, there is no limestone or chalk in the immediate neighbourhood. Probably one would have to go to Derbyshire to obtain the necessary calcareous material.

This brings us once more to the fundamental question of having the three requisite factors: (1) something argillaceous, (2) something calcareous, and (3) source of power, all within easy reach of each other.

In an earlier part of this book I have touched lightly on the possibility of electrical means of bringing cement raw materials to a clinkering temperature, and have said that that is a matter rather of the future than the present.

What has been said there does not apply to the utilisation of electrical power for driving all parts of modern cement plant. As the cement industry is typically English, it is in the condition

of Topsy, who said, "Specs I growed," and it is precisely on account of this that the most diverse methods of obtaining and utilising power have been employed, with more or less success in this pioneer country, and at this moment there is no regular or standardised practice.

By the courtesy of various manufacturers, whose information is suitably acknowledged, I have been able to correlate, with my own knowledge, something of their commercial experience.

The best description from a manufacturer's point of view of the generation and distribution of power electrically has been afforded me by Messrs. Allen of Sheffield. Mr. Coles, who has charge of this part of the plant, contributed two articles to the *Electrical Review*, from which I quote freely and with full acknowledgment.

Mr. Coles says: "Both the horse-power installed per ton of annual output and the energy consumed are now much greater than before." This is true and may be accepted with the reservation that horse-power relates only to that of machines; the total horse-power will, of course, include the number of units of energy contributed by manual labour, and as this, in an old-fashioned works designed before the rotatory process was thought of, was exceedingly great, and is not exactly known. It will be understood that a proper computation of the total units of energy put side by side with the units from the mechanical prime movers is the only way of saying whether or no the present method needs more or less horse-power than the older does. Mr. Coles's excellent paper goes on: "The latter, however, has increased at a greater rate than the former, with the result that the load factor has been materially improved." The natural deduction from this is that a point is within reach where power can be taken from a public plant more cheaply than by the installation of a private generating plant. I will quote another paragraph from this article almost in its entirety, adding my comments.

"A rotatory kiln installation . . . consists almost entirely of moving machinery, which includes the kiln itself, the coal mill, the fans for air and coal, the clinker cooler, and elevating and conveying gear. These in the aggregate may require from 60 to 140 h.p. per kiln, depending upon its size and output. A second reason for the increased demand for power lies in the fact that modern specifications call for much more finely-ground cement, with the consequence that for any given output per week the grinding machinery has to run considerably longer

hours or be increased in capacity. In addition to the finer grinding of the cement clinker that has now become necessary, it has become the custom to reduce the raw material before burning to a much greater degree of fineness in order to ensure the cement passing the severe tests usually called for as regards soundness and freedom from expansion." It must be remembered that this article represents the practice of 1911, and at that date the absolute necessity of producing a perfectly sound cement was less understood than it is now, when the labours of the Cement Committee of the British Engineering Standards Association have come to fruition. There is another interesting paragraph in the same article which is certainly worthy of quotation.

"The kilns are mounted on rollers with an inclination of 1 in 20 to 1 in 30, and are rotated at a speed of from $\frac{1}{2}$ to $1\frac{1}{2}$ revolutions per minute, the size of the motor installed to drive the kiln only varies from 15 to 30 h.p." I agree with this estimate, making allowance for the larger size of the modern kiln—say 200 ft. in length and 10 ft. 6 in. diameter at the burning zone—and taking into account the better mechanical construction of the whole affair, both as regards the rollers and the bearings which take up the thrust, and the better alignment of these respectively. I consider that, even with large kilns, 30 h.p. is not far out. It must be quite understood that there are plenty of plants in which this horse-power for kiln-driving proper is much exceeded, and it can generally be found that the excessive consumption of power arises either from bad design of the kiln or from accidental inclusion in the horse-power, as returned, of portions of the plant subsidiary to the kiln, such as the coal mill, fans, and the like. In the paper, from which I quote, there is an interesting table which, with full acknowledgment to its author and *The Electrical Review*, I quote below.

MACHINE.	H.P.
<i>Raw Material Mill—</i>	
Chalk crushers	7'20
Wash mill	20'50
Wet ball mill	25'50
Wet tube mill	35'65
Slurry mixer	8'30
Slurry pump	6'18

MACHINE.	H.P.
<i>Rotary Kiln Plant—</i>	
Kiln	8'30
Clinker cooler	3'10
Fan	5'18
<i>Coal Mill—</i>	
Drying drum	4'10
Ball mill	15'35
Tube mill	30'60
Pendulum mill	20'35
<i>Cement Mill —</i>	
Ball mill	30'65
Tube mill	50'100
Pendulum mill	30'50

As this paper frankly admits an advocacy of electrical driving, it is fair to quote the following—

“ The chief benefits to be derived are as follows—

(1) The engine-room can be located in any part of the works independently of the position of the running machinery.

(2) The various departments can be located independently of each other, and of the engine-room.

(3) Variable speed for particular machines can be easily and economically arranged for.

(4) Any department can be shut down at will without, as is often the case, running long lengths of idle shafting for considerable periods.

(5) In the event of one engine being shut down owing to an accident or repairs, the remaining engine (where two are installed, which is usual) can supply power for whichever department it is most important to keep running at that particular time.

(6) The works can be extended in the future with a minimum of expense and trouble, both in the initial stage and later on when additions are required.”

The second section of Mr. Coles's paper is also of considerable importance and well worth quoting. He advocates the use of a separate motor for each Kiln, and there is a good deal to be said for this. But it must be remembered that the advantage gained of closer control of the speed of the kiln obtainable when each is driven by its own motor is scarcely necessary, as a kiln, if running regularly both from the feed end and the fuel end,

needs little variation in speed, and if an alteration has to be made it is rather in the nature of stopping and starting than careful graduation of rate of rotation. The one thing essential in rotatory cement practice is regularity in every respect, and all devices for altering the procedure are a tacit acknowledgment of irregularity of conditions. It is most useful to have at disposal the flexibility of an electric motor if the conditions are irregular, but it is far better so to arrange the plant that irregularity is so rare as to make the flexibility superfluous. The question of continuous running is touched on, and that may be considered at once in general terms. In an ideal cement works the whole plant will run 24 hours a day, 7 days a week, and 365 days a year with an extension of 1 day in leap year. As in practice this is not attainable, a useful approach to it is to run the kilns 168 hours a week, and to provide power for their running continuously for that time. On account of needs for repairs of linings and the like the 168 hours will not be reached, and on account of the necessity for repairs of other plant this deficit will be accentuated.

It is interesting to note that the air supply for the kiln is sometimes provided by a steam injector. The author has not seen such a plant, but regards it as quite possible, and possibly economical, and in any case it is certainly convenient. It must be quite understood that the fundamental idea of pushing powdered coal into a kiln so as to make a blow-pipe flame originated with the Hurry & Seamens plant at Northampton, Pa., and it must also be understood that, mechanically beautiful as the plant was, it is an impracticable process because of the heavy cost of the compressors both in capital and running. There may be such plants running now, but in cases within the author's knowledge the majority have been pulled out and the fan substituted. Here it may be worth recording that the northern parts of Europe, including Germany, took the lead, abolished the high-pressure system and blew in the coal-dust holos-bolos by a fan; that was as long ago as 1900.

Reverting for a moment to Mr. Coles' able article, it is satisfactory to note that he recognised the necessity of separating the prime mover from the driven plant. An instance is given which may well be quoted: at the Stern cement works of Messrs. Toepffer Grawitz & Co., near Stettin, with which the writer is well acquainted, there has been installed a new power plant which consists of a 1200 h.p. condensing engine fitted with a rope

drive and driving the cement mill direct. On the crank-shaft is a 350 K.W. 500 volt D.C. generator, which supplies power for the rotatory kilns and the raw material plant. The second example of methods of driving is given in the same article, in that the engine-room is situated between the cement mill and the raw-material mill. The writer of the article properly points out that in cement plant a large starting effort is usually required, and quite properly adheres to the view that an electrical system may have many advantages. But it must be remembered that the difficulties of using clutches may be overrated, and that the greater simplicity and relative cheapness of a mechanical drive may well compensate for the comparative complexity of what is really the same thing, that is the slip of an electrical clutch.

One of the interesting points made in these two articles accords very well with my own experience. I have always regarded a $\frac{1}{2}d.$ per Board of Trade Unit as about the figure at which a cement works can be run from a local generating station, and Mr. Coles says, "It may, generally speaking, be taken that unless a supply can be obtained on such terms that the price per unit will not exceed from $0.4d.$ — $0.6d.$ it will be more economical to generate on the works."

Corresponding information is given by other manufacturers, whose statements, being at first hand and based on actual practice, I do not hesitate to quote, with their consent.

Messrs. Smidth's information goes to show that just as the consultant has to judge everything on its merits, so the manufacturer cannot be wedded to any particular system without prejudice to efficiency.

Messrs. Smidth says: "Years ago it was a common practice in this country to have one engine installed for driving one part of the factory, such as the wash mills, and one engine for driving another part containing, for instance, the clinker grinding mills, and so forth. Later on the tendency was to substitute the small engines by one large engine which then gave off power to large transmissions which drove, by means of ropes and pulleys, the mills, etc."

This alteration I have seen myself, and it fairly describes part of the evolution of the important item of power production in the modern cement mill. In the olden days various small engines, uneconomical and often placed in highly inconvenient places, were the characteristic style of plant, and later on a majestic engine, usually of the cotton-mill type, was made

responsible for the whole output, aided, of course, by one or two satellites for special purposes.

Messrs. Smidth proceed thus: "During the last few years practically all new cement factories have been arranged for electrical driving, the electricity being generated at a power station common to the whole works." This is a natural corollary of the suggestion that a central power station, represented by the ordinary mill engine, is desirable in a works where the distribution of power in an economical fashion is as important as it is in a cement works, but in my view there are limitations, and if a balance sheet of power to cost of cement produced were set forth showing not merely the total cost of power, but including such difficult items of the ultimate cost to the manufacturer involved in the run of more complicated machinery needing more skilled handling, it might be found that there is much to be said for the older methods. It must not be supposed for a moment that I pin myself to any particular form of prime mover or of drive. As I said above, each case must be considered on its merits.

It has been my object throughout this book to obtain the opinion of those concerned with the construction of plant and to set that opinion down as fairly as I can, not hesitating to say that sometimes I disagree, but the brief summary of Messrs. Smidth's communication fairly represents my own view, with the necessary reservation as to the consideration of local conditions.

I have been favoured by similar information from Messrs. Ernest Newell & Co., Ltd., who, while pointing out that primarily they are makers of cement plant as distinct from power plant, have nevertheless necessarily had a large experience of the nature of suitable power plant and the quantity of power normally required.

A few quotations from their communication may be of service.

"The power required in an up-to-date cement factory is something between $1\frac{1}{4}$ to $1\frac{1}{2}$ h.p. per ton of cement per week, *i. e.* for an output of 1000 tons the motive power for machinery only—that is, exclusive of electric lighting, haulage and quarry work—would be something like 1250-1500 h.p., depending upon the class of machinery used and the nature of the materials which have to be ground."

"In the case of large works, where water is available and where bituminous coal can be bought at a reasonable price, the most economical method is to use turbogenerators, whilst in

smaller plant, say of 500 tons a week output, gas engines and producer plants can be satisfactorily used."

I may say at once that I regard the statements as sound. The allowance for power is on the liberal side, but there have been so many troubles caused by cutting the power too fine that some extra capital expenditure will probably be recouped in the long run, and it must always be held in mind that with larger kilns and with finer grinding the minimum power which it is safe to reckon on must increase. There are several other remarks in this valuable letter, giving as it does the views of a manufacturer of high standing, which may be summarised thus:—In a works put down so recently as to be unhandicapped by old plant or old traditions, the plant installed consisted of two 1500 kilowatt alternating current machines, 3 phase 50 cycles, provided by steam from water tube boilers mechanically stoked. The importance of excluding dust from the engine-room and the motors is also emphasised most properly. Those who can remember cement works of the olden type, where the engine-room served as a sort of reservoir for all the dust of the works which did not go up the flue or down the throats of the workmen, will appreciate this point. It was general abroad some fifteen years ago, but was not so fully recognised here; the advance is a substantial one. Initial expense of dust collecting was always the bogey, but now it is generally recognised that *cleanliness pays*.

On the whole the question of power plant for cement works resolves itself into this: there must be power plant, of whatever sort, capable of running smoothly throughout the year of 365 days, each of 24 hours; in short, the old muddly methods are hopelessly out of date. The plant must be certain in its operations, as a really good plant is, for the production of such chemical materials as aluminium and calcium carbide; nothing short of this will do. The old methods of driving, by horizontal engines driving any kind of plant which was under continual need of repair, are obsolete. There comes in here an important economic question, that is, the question of labour. Most happily, by the ability of the engineer, the labour trouble has almost disappeared. I well remember the time when labourers, working in a mill-room where clinker was being ground, used cloths over their noses to protect them from the caustic dust in the atmosphere in which they had to work. All this is gone, and the present conditions of manufacture are wholly different. The proportion of power to cost per ton of cement has already been given, and the reasons

for its increase have been indicated. There is little doubt but the proportion will again decrease,¹ as there is no physical reason why clinker should not be ground with an almost negligible expenditure of energy. To tear one particle of clinker from another truly requires some expenditure of energy, but is small compared with the energy put into the material in the act of burning. In fact, clinker may be looked upon much as is glass in a state of internal stress, which may be disintegrated spontaneously by the action of these internal stresses. Exactly the same thing happens when clinker "falls." The clinker is reduced to dust without the application of any external energy. It follows that clinker in a state of stress can be ground to the relatively coarse powder which we call cement with a minimum expenditure of energy.

I discussed this question with Mr. Davidson of Messrs. Smidth in Copenhagen some ten years ago, and he, as the deviser of the tube mill, was disposed to dispute it. I do not know whether I convinced him, but the issue is clear. If the particles of any substance hold together, it may be taken that it is so by molecular attraction. It is impossible to separate molecular particles from particles by any mechanical means, but the separation of large pieces, as large as those which pass through a 200-mesh sieve, may be and is so effected. But the expenditure of energy necessary for this is negligible, as any one knows who has crushed a brittle material such as quartz or diamond. The bulk of the energy expended in grinding either clinker or cement raw materials is due to the inefficiency of the machines, and I suppose that it was on this ground that Mr. Davidson and I differed. By inefficiency I do not mean any want of mechanical accuracy in the mechanism. They are admirable machines. What I wish to be noted is that, quite apart from the inevitable expenditure of energy in tearing asunder fragments of a mass, there is a much larger expenditure of energy in rubbing round the balls in the mill and making them impinge upon and break up the pieces of clinker which are to be comminuted. Some sage said wherever there is noise there is loss, and this applies to all things, including ball mills and politicians. Those who have been in a big cement mill know that the noise is deafening, but it is only an index of the real loss, which can be easily reckoned from the horse-power necessary to turn out so much stuff per hour, deducting merely

¹ This was written before the idea of labour being entitled to all profits became common.

that needed to rend the particles asunder—a negligible quantity. Unfortunately this fact is not generally recognised, and, as in many other cases, the heat is regarded as irrecoverable because it is at a relatively low temperature. It is to be feared that with our present physical knowledge, which has not been able to provide so simple a thermal machine as an SO_2 engine to work commercially, this must be accepted as true, but that is no reason why the problem should not be tackled from the other end; that is to say, that a method should be devised to make the relatively coarse powder called cement with but little more expenditure than is necessary to tear asunder the few molecules which are opposed to each other on a given cleavage.

This idea was clearly in the mind of the late Mr. Ransome, who shares with Navarro and one or two others the credit of conceiving the rotatory kiln as a practical device. In his original experiments it is obvious that he expected cement ready ground to be producible from slurry ground to the same fineness, and thus he hoped to avoid the costly process of grinding. He shared the ignorance of the time, which regarded the burning of slurry to cement as a kind of ceremony instead of the essential step in the proceeding; this was due to pure ignorance of chemistry. Quite apart from the many mechanical defects of his plant, the fact is plain that he had no proper conception of kiln chemistry. All honour to him that he laid a foundation stone for the modern method of making Portland cement by the rotatory process.

Reduction of the total power needed to reduce one ton of clinker to its equivalent weight of cement is a pressing problem. Something has been done by Mr. Edison in the way of percussive rollers, and if clinker were only hard and brittle, these might serve. But unfortunately it is also tough—extremely tough—and for its comminution needs much power. Lead is a soft metal, mechanically weak, but to grind lead to a fine powder is an almost impossible task. It is best to put aside all conventional methods and consider the problem on its merits. As far as I know no one has tried whether clinker is more or less brittle at a low temperature, and correlatively whether there is some higher temperature at which the material becomes brittle. In the latter case, zinc is an example, for at the ordinary temperature it is fairly tough, and when heated to about 250°C . becomes brittle enough to break up in a mortar.

A similar line of thought is provided by the case of tin, which is tough at ordinary temperatures, and goes to pieces spon-

taneously if long exposed to temperatures below freezing-point, the two materials being allotropic. It is on such lines that the problem should be attacked, it not being accepted that conventional methods, however good, are final. It would be well worth while to make a complete series of researches on this very point. Supposing it were shown that "Coolth," as my friend James Swinburne says, is the remedy for the warmth generated by the ordinary friction of grinding, it may well be that the cost of "coolth" will be smaller than the cost of useless warmth. The alternative is to utilise the warmth, *i. e.* low temperature heat, and at the present time this is not attempted. In point of fact the sources of heat in this and other countries are too cheap and abundant to encourage any economising; the whole question is considered on a purely *£ s. d.* basis, and provision for posterity is disregarded. This is a sound principle, always provided that obviously avoidable waste is prevented. When solar heat is taken into account the matter assumes a different aspect. On every unit of area of the earth's surface a quantity of energy is poured—computed by the ingenious—but without paying too much attention to their calculations it remains certain that the total amount is gigantic. Naturally, most of it falls in the neighbourhood of the equator, which is just where it is not wanted for civilisation, as we know it. Man has almost conquered land and sea, and has very nearly conquered the air; that conquest is certain and near. His next task is to conquer the "Ether" and deflect any rays, whatever length they have, whether those of light or Hertzian, and to deflect them as he pleases. This done, energy could be switched from the tropics, where it is merely wasted on growing useless jungle and is an incentive to idleness, to higher latitudes, and used to make a temperate climate therein. Equally the tropical belt would become possessed of a temperate climate, so that the advantage would be correlative. There would probably be a balance which could be used as a source of power nearest to the place where the raw materials existed. It would be greatly cheaper to shift sunlight power, than to move chalk and clay to a source of power. The converse is equally true: it is cheaper to move chalk and clay to a waterfall than to cart a waterfall to, we will say, Rugby.

From whatever aspect one regards the comminution of cement, one fact stands out, namely, that it is a costly operation, altogether out of proportion to the result obtained. The same, of course, may be said of the grinding of the raw materials, which

brings us back to the question, What is the expenditure necessary for making properly burnt Portland cement? The all-important item is the decomposition of calcium carbonate and the formation of silicates and aluminates of calcium. Whatever improvements are made, that must be reckoned with. In carrying out this essential reaction a great deal of surplus heat is produced according to present practice. It should be sufficient to run the whole plant both for drying and grinding, and I look forward to the time when a cement kiln without means of picking up the surplus heat will be as obsolete as a blast furnace without a stove for heating the blast.

CHAPTER VI

WORKS CONTROL

UNDER this heading it is usual to consider only the chemical control of the various materials used, and this chapter deals with "works control" in this narrower sense, and not in the broad one of control of works which the title might suggest. The first thing of importance is that of sampling, and it is difficult to over-emphasise this—as bad sampling has caused a lot of trouble. The sample must be representative of the bulk, and it is of little use taking one small piece of shale from the top of a truck, and saying that it is a sample of the truck load, particularly if the material is irregular in composition. If the materials are in lumps, several lumps should be taken and crushed up. Great care must be exercised in seeing that the lumps selected contain the proper proportion of any foreign matter (veins, etc.) contained in the bulk sample. The crushed material is then mixed thoroughly and "quartered down," taking care that there is a proper proportion of coarse and fine. This is then ground, and if the sample is still too large, it is mixed and "quartered" again before the final grinding.

Because of the importance of obtaining a proper sample it is strongly advisable that the chemist should know the raw materials at their source, also their nature and the limits of variation, as the precautions to be taken will depend largely on this. If the materials are very even there will not be much difficulty, but if there are small "faults" which are not sufficiently large to reject, the greatest care is necessary.

Rapid methods, giving reasonable accuracy, are usually better for the purpose of "works control" than more accurate but slower ones. In this chapter, therefore, the methods stated will yield results sufficiently accurate for the purpose, whilst for closer work the reader is referred to the methods given in the chapter on "Analysis."

Each chemist will be able to say how much work is necessary to keep control of his particular materials, and will arrange

accordingly, but in a general way the number of samples described below, with their treatment, will usually be sufficient to maintain control and furnish all that is necessary for the works record.

The *calcareous materials* (chalk, limestone, marls, etc.) should be sampled from time to time.

All that is necessary as a matter of routine is the estimation of moisture, and then the quantity of carbonic anhydride in the dried sample, with an occasional complete analysis as a check.

For moisture, from 10 to 50 grms. of the powdered sample is dried for an hour or two in an air bath at 105° C. to 110° C., cooled in a desiccator, and weighed. If the sample is wet, care should be taken to see that as little moisture as possible is lost in grinding, also, as a drying oven is not always available for drying, the operation may be carried out on a hot plate or in any other convenient way, so long as the drying is thorough and the material not overheated.

The carbonic anhydride is estimated by means of a calcimeter, or by titration, both of which are described fully when dealing with slurry. The method for analysis is given in the chapter devoted to that subject.

The siliceous materials (clays, shales, etc.) are sampled from time to time, and the moisture and combined water estimated, and sometimes the silica, alumina and iron oxide, and lime are also estimated; occasionally a complete analysis is required.

The moisture is estimated by drying a weighed portion of the sample in an air oven at 105° C. to 110° C. For combined water 0.5 or 1 gm. of the dried sample is ignited at a dull red heat for half an hour, cooled in a desiccator, and weighed. Instead of the dried sample, the ground undried portion may be taken, a correction being made for the moisture present. Should the sample contain pyrites, or iron in the ferrous state, this method will not give correct results. If, however, these remain constant, the method may be used under "Standard" conditions, as the error will be more or less constant, but if accurate results are required, the method given in the chapter on "Methods of Analysis" (p. 175) should be used. The main constituents are estimated by a simple fusion: 0.5 gm. of the dried sample is fused with 2 to 3 grms. of pure sodium carbonate in a platinum crucible, the melt is transferred to a dish digested with hot water, and dissolved in hydrochloric acid. When solution has been effected, with the possible exception of a few

flakes of precipitated silica, the whole is evaporated to dryness on a triangle on a hot plate, covered, and baked for an hour. The dish is allowed to cool, and the residue digested with the hydrochloric acid, diluted and filtered. The silica is washed, dried, ignited at full temperature of the muffle for an hour, cooled in a desiccator, and weighed. To the filtrate a small quantity of bromine water is added, and then an excess of ammonia. The whole is digested, just below boiling-point, for fifteen to thirty minutes, until the solution has only the faintest smell of ammonia, when the precipitate is filtered off, washed with hot water, dried, and ignited in the muffle, etc. This precipitate will contain all the alumina, iron oxide and manganese oxide, and the lime and magnesia will be in the filtrate. If these latter are small, they can be neglected for the present purpose, but if large, the lime is estimated by means of oxalate, and the magnesia by phosphate.

When a complete analysis is required, it may be carried out by the method described in the chapter on "Methods of Analysis."

Slags.—The estimation of moisture and the occasional estimation of the main constituents are all that is necessary as a matter of routine.

Sand.—An occasional chemical analysis is required. A mechanical analysis should be made on each delivery.

Slurry and Raw Meal.—The main, and perhaps the most important, duty which comes under the heading of "works control" is the maintenance of control of the slurry in a wet plant, and the raw meal in a dry plant. It is, of course, essential that the composition of these should be kept within narrow limits, and as they consist of mixtures of two or more different materials, the samples should be taken frequently, in order to be able to correct any error directly it occurs. The fineness of grinding is of almost as much importance as keeping within the narrow limits of composition, and the frequent sampling of the slurry or raw meal enables a constant control of the grinding to be maintained. The place where the samples are taken will vary according to the plant, whether it is wet or dry, etc., and the frequency will vary according to the local circumstances and output, but if the methods adopted in a fairly large works using the wet process, and in another using the dry, are stated, they will give a clear indication of how the control is maintained.

In the case of the wet process, two samples are taken every

half-hour, one from the wash mill, which is sufficiently early in the process to enable any necessary correction to be made, and the other from the mixing tanks, to see that the final mix is of proper composition.

Similarly in the case of the dry process two samples are taken every half-hour, one from any convenient spot giving the average of mixed output from all mills, to enable any error to be detected at once, and the other from any convenient point where the final raw product can be taken, which in this particular works is the kiln feed. Each sample is examined (1) for its content of carbonate, (2) for its fineness, and (3) occasionally a portion of each sample taken from one point over some hours is bulked and analysed.

In determining the fineness of grinding of a slurry, a known volume, 100 c.c. or so, is taken and washed through a 180×180 mesh sieve, and the residue dried and weighed, also the weight of dry material in the same volume of slurry must be determined, if it is not already known. The weight of the dry residue which is too coarse to pass the sieve should not be more than 4 % of the dry material of the slurry. In the case of raw meal, 100 grms. is sieved through a 180×180 mesh sieve; the residue should be as low as possible and not exceed 4 % in any case. Fine grinding is essential in order to bring the various constituents sufficiently close together for them to combine. The water in the wet process greatly assists in mixing and bringing the particles close together, but in the dry process fineness of grinding has to be relied on, hence it is still more important to insist on fine grinding for the latter than for the former.

The estimation of carbonate, by means of a calcimeter, etc., or any other method, is made more for an index of the composition than to give the actual composition of the mix. By this means only the quantity of calcareous matter (and magnesia) present as carbonate is determined, and any calcium silicates present would not affect the estimation, but would nevertheless have an important influence on the composition of the cement. As an index, however, this does not matter, as once the percentage of carbonate contained in the mixture producing the quality of the cement required is known, all that is necessary is to keep the amount of carbonate within certain limits of the known figure to be reasonably certain of producing a cement of the same composition.

In all cases it is necessary to dry the samples before estimating

the carbonate. With slurry, it is usual to dry a small quantity on a hot plate or any other convenient place, but as there is a danger of insufficient drying on the one hand, or of overheating on the other, it is better to do it properly and dry it in an air oven at 105° C. to 110° C.

Although the estimation of carbonate for "works control" is usually carried out by means of one of the various types of calcimeter, other quick methods, such as titration, may be used, so long as the results are reasonably reliable.

Of the various types of calcimeter only two will be described. The first is that due to Dr. Scheibler; most of the calcimeters on the market are but modifications of this. The second is Clarke's, and is one of the latest and most satisfactory calcimeters in use at the present time.

The illustration of Scheibler's calcimeter (Fig. 50) shows the construction of the apparatus. The principle is as follows: The small bottle contains the material to be tested, and also a tube containing hydrochloric acid. When all the corks and stoppers are fitted gas-tight, this bottle is gradually tilted until the acid flows over on to the material, when the readily attackable carbonates will be decomposed, with the liberation of a corresponding amount of carbon dioxide. This will cause the bladder in the next bottle to expand, and consequently displace a certain amount of air outside the bladder, which in its turn will depress the water in the large graduated tube. This water will flow up into the other tube, which is not graduated, and will cause the whole to be under pressure; therefore before a reading of the volume of gas is taken it is necessary to let the water out of the plain tube until it is level with the water in the graduated tube, when the whole of the gas in the apparatus will be under atmospheric pressure. Provided the apparatus had been properly set at the beginning, this final reading will give the volume of carbon dioxide, less the amount left in solution, and with suitable corrections for this, and also for temperature and pressure, the weight of carbonate can be calculated. This apparatus is liable to give erroneous results, owing to differences of temperature between the thermometer and the graduated tube, and also any variation of temperature of parts of the apparatus during the estimation. This has been overcome to a large extent in Clarke's calcimeter by enclosing the whole apparatus in a water jacket. This apparatus is illustrated in Fig. 51. The principle is the same as in Scheibler's apparatus.

in that the gas which is liberated by the action of acid on the carbonate indirectly displaces a corresponding volume of water, but in addition to the water jacket various other improvements have been made. The bladder has been done away with, and a

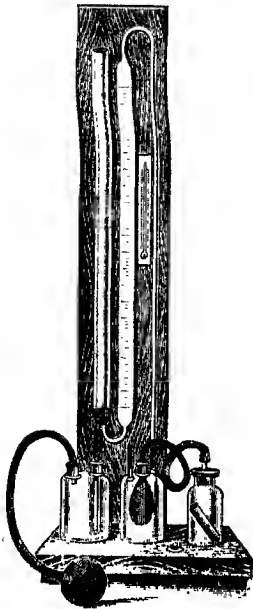


FIG. 50.—Scheibler's Calcimeter.

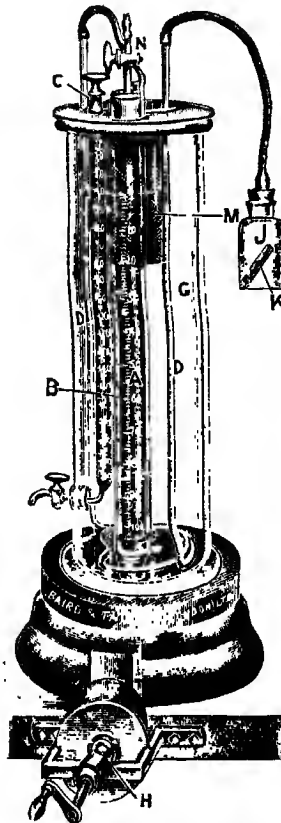


FIG. 51.—Clarke's Calcimeter.

coil introduced, the carbon dioxide having direct access to the body of the apparatus. The graduated tube is concentric with the plain one, which simplifies the levelling process, and the fine adjustment of this is further assisted by means of a bellows fitted on the stand, which has a screw adjustment.

A burette for holding the hydrochloric acid is also enclosed in the water jacket, so that the acid used may be of the same temperature as the rest of the apparatus.

The method of working this calcimeter is as follows: the water jacket, tubes A and B, and the nearly closed bellows are filled with water, care being taken to see that no air is left in the bellows, and the joints are tested to see if they are gas-tight by closing cock N and opening the bellows until there is a good difference of head between A and B, when any appreciable leak will reveal itself, and can be put right. The water level is then restored. A weighed portion of the dried material (the quantity is indicated in a table) is placed in the bottle J, and 10 c.c. of hydrochloric acid (sp. gr. 1.112) is run into the tube K, and carefully placed in the bottle, which is then closed with its stopper, and immersed in the cage in the water jacket. As soon as constant, the temperature is taken, and the water in tubes A and B is adjusted by means of the bellows and cock N, until they are level at the zero mark. The bottle J is then taken out and tilted so that the acid comes out slowly, and while the carbon dioxide is being liberated, the bellows F is slowly opened so as to keep the water in B nearly level with that in A. When the reaction is complete, the liquid in the bottle is swirled round for half a minute to expel the excess of gas from the super-saturated solution. The bottle is then placed in the cage in the water jacket to cool for a couple of minutes or so, and the water in A and B is levelled once again and the reading taken. (If the water jacket is at room temperature, there will be no appreciable alteration during the experiment, but if it is either warmer or cooler, it will be necessary to adjust to the same temperature as when the apparatus was set to zero.)

The volume of moist gas obtained must now be calculated to its equivalent weight of calcium carbonate, corrections being required for the pressure, temperature, moisture, and the amount of gas in solution in the apparatus. This calculation is practically done away with by means of tables supplied with the apparatus, which furnish all the necessary corrections. It will be understood that all such methods, though useful and necessary for "works control," are not absolute.

The calcimeter, by the fact that it is used cold, is limited to the estimation of carbonates easily decomposed by hydrochloric acid in the cold, and hence is not of much use for dolomites, or samples where the estimation of magnesium carbonate, etc.,

in that the gas which is liberated by the action of acid on the carbonate indirectly displaces a corresponding volume of water, but in addition to the water jacket various other improvements have been made. The bladder has been done away with, and a

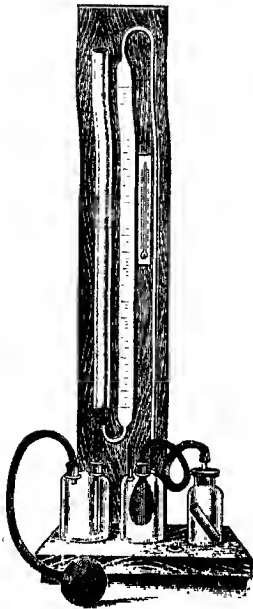


FIG. 50.—Scheibler's Calcimeter.

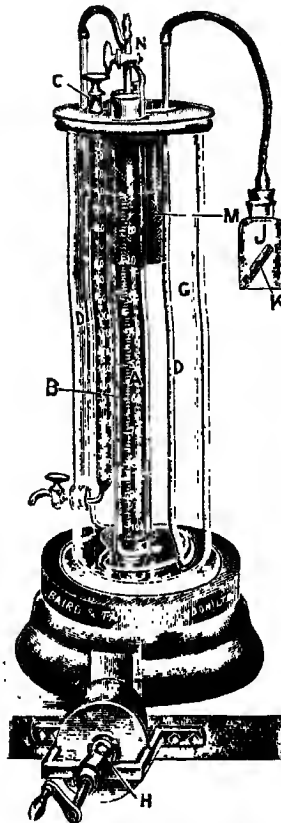


FIG. 51.—Clarke's Calcimeter.

coil introduced, the carbon dioxide having direct access to the body of the apparatus. The graduated tube is concentric with the plain one, which simplifies the levelling process, and the fine adjustment of this is further assisted by means of a bellows fitted on the stand, which has a screw adjustment.

acts as a safeguard in this method against loss of acid through boiling. When a strong solution of hydrochloric acid is boiled, the acid boils off, leaving the water behind until a certain strength acid is reached, when both acid and water will boil off together. When a weak solution of hydrochloric acid is boiled, it is the water and not the acid which goes off, until this certain strength is reached. As in this method the solution which is boiled is very dilute, the simple form of condenser, viz. a plain tube, is sufficient to prevent hydrochloric acid being carried away with the water.

From time to time an analysis of the slurry should be made, and for this purpose equal parts of the half-hourly samples—say from the mixing tank—are taken and thoroughly mixed, dried and ground. One grm. of this dried material is ignited in a weighed platinum crucible for an hour at the highest temperature of the muffle, cooled in a desiccator, and weighed, this giving the loss on ignition. The ignited material is transferred to a dish, broken up with a glass rod, and dissolved in a little water and hydrochloric acid as for a cement. If the original mixture had been finely ground and the burning properly done, there should be practically no insoluble matter, and the analysis may proceed on exactly the same lines as that described for cement in the chapter on "Methods of Analysis." If, however, there should be a large amount of insoluble residue left, it shows that the reaction between the calcareous and siliceous materials has not been complete, and it will be better to reject this portion and start afresh, taking precautions to see that the material is finely ground and the burning sufficiently thorough.

The chemical composition of the raw materials will have a great influence on the burning of them in the kiln, but as the question of burning scarcely comes within the scope of "works control," it need not be discussed here. As soon as they are burnt, however, they come within the range of the "works control" again. The clinker, as it leaves the cooler, is usually quenched, and is then conveyed to the mill or to the clinker bank, and it is whilst it is on its way to the mill that the regulation of the setting time of the finished cement is taken in hand, if gypsum is used for the purpose; or whilst it is actually in the mill, if the regulation is by steam. The effect of gypsum on the setting time of Portland cement has been discussed in an earlier chapter, and this effect is utilised for slowing the setting time of fresh cement by adding 1 % or so of calcium sulphate, in some form

or other, to the clinker before it goes into the mill. This gypsum or other form of calcium sulphate is sometimes weighed out and fed in by hand, but in the majority of cases it is fed in from a feeding-table, and the quantity is regulated to a nicety. This property of regulating the setting time is not altogether reliable if the cement is likely to be stored, and other methods have been tried. The most successful of these methods on a commercial scale is one due to H. K. G. Baumber, the method being to blow steam into the tube mill whilst the cement is being ground, and which apparently hydrolyses some of the less stable aluminates as well as slaking any free lime which may be present. The steam increases the temperature in the tube mill caused by friction during grinding, until it is just below 100°C. , consequently the cement does not become wet in the ordinary sense, but leaves the mill in the form of a dry powder containing about 1 % of water. The setting time is considerably retarded by this process, and further regulation may be made by small quantities of gypsum. In addition to this, the steaming process appreciably improves the soundness of the cement.

Control of the finished cement is maintained by testing samples, taken from the mill spout every half-hour or so, for fineness and setting time, and also by bulking the samples and testing for soundness every four hours or so, and making a complete test for tensile strength and analysis every twelve hours. The frequent testing for fineness and setting time allows of the early detection of any change due to overrunning in the case of the tube mill, or to a broken screen in mills which use screens, and also of any alteration in the quantity of gypsum, etc., necessary to obtain the desired setting time. The less frequent tests for soundness and tensile tests are made on the fresh unaerated cement, and because the cement has not had time to "ripen," these tests may be looked upon as very stringent, and if the cement passes them, the probability is that the cement will be still better by the time it is used.

The above analyses and tests are made for the purpose of "works record," and are carried out by the methods described in the chapters on "Analysis" and "Testing," but when a "parcel" of cement is sold it is usual for it to have to comply with the requirements of the British Standard Specification, or occasionally a modified Specification, and for this purpose a sample is taken from the "parcel" as distinct from a sample from the mill spout, and is tested in strict accordance with the specification.

The "parcel" of cement is sampled by hand or by some mechanical device. For sampling by hand, holes are dug in various parts and a small quantity of cement is taken from each hole and mixed. The mechanical devices are many, of which three examples may be given. The first is on the principle of the Archimedean screw, whereby portions of cement are brought up from various parts of the heap, and then bulked. The second is by means of a hollow rod sealed at the bottom, but having a little hinged door two or three inches from the end. This rod is pushed into different places of the heap with a slight twisting movement to keep the door closed, and when

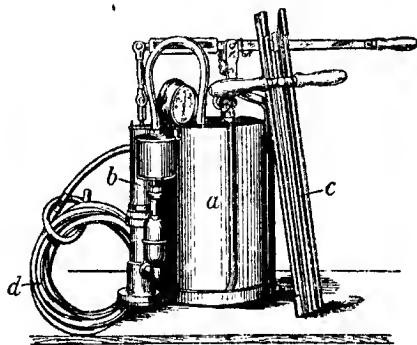


FIG. 52.—Cement Sampler.

sufficiently far in, the rod is twisted in the opposite direction and the door opens, letting in the cement, when the door is closed by a twist in the opposite direction, and the rod containing the cement is withdrawn. The third method is perhaps the most satisfactory, and depends on a vacuum for drawing up the cement. The apparatus, illustrated in Fig. 52, consists of a vacuum chamber *a*, connected with a pump *b*, or other means of obtaining a vacuum, and a set of screwed tubes *c*, together with a flexible connection *d*, between the chamber and the sampling tubes. A man-hole is provided at the top of the drum for emptying. The sampling tube is pushed into the cement to any desired depth, and, on pumping out the air, the cement flows into the drum; this can be repeated at any number of places in the heap. Experiments have shown that the sample taken by this method is truly representative of the

bulk, and contains the true proportion of coarse and fine cement.

There are various other materials, such as coal, water, oils, etc., which come within the scope of "works control," and which have to be examined.

Coal.—The coal, as it arrives, is sampled so as to represent the bulk, and this sample is broken down—not ground—till it will pass through a 30×30 sieve, and examined for its moisture, ash, volatile and fixed carbonaceous matter, calorific value, and sulphur content.

The composition of coal is such that no definite point can be obtained which will give the end of the evaporation of moisture and the beginning of loss of volatile matter, so it is necessary to fix some arbitrary conditions for carrying out the estimation in order to get anything like concordant results. A similar sort of thing occurs with the determination of volatile and fixed carbonaceous matter, and so for both of these estimations standard conditions have been evolved and are generally accepted.

For moisture, 1 grm. of the powdered coal is weighed into a crucible, and dried for exactly one hour in an air bath at 104° C. to 107° C. In the case of the coal being wet, the moisture should be determined on a coarsely crushed sample as well, and if more than that of the fine coal, as it probably will be, all other determinations made with the fine coal should be corrected accordingly, if accurate results are required.

For volatile and fixed carbon, 1 grm. of the undried powdered coal is weighed into a large platinum crucible, fitted with a close-fitting lid, and weighing from 20 to 30 grms. The crucible is placed on a platinum triangle and supported above a large Bunsen burner, capable of giving a flame at least 20 cm. high. The bottom of the crucible is to be from 6 to 8 cm. above the top of the burner, and the crucible and contents are to be heated exactly seven minutes with the gas full on in a place free from draughts. The lower part of the lid will be found covered with carbon, and this should be allowed to remain, but the upper part of the lid should have been burnt clean. The crucible is cooled and weighed, and the difference in weight, less that due to moisture, gives the amount of volatile carbonaceous matter. The residue in the crucible consists of fixed carbon and ash, and by deducting the weight of the ash, which

is more easily obtained on another portion, the amount of fixed carbon is obtained.

For ash, the portion used for the estimation of moisture is taken and ignited in an open crucible over a Bunsen burner, at first very gently, and increasing the flame as the ignition proceeds. When the carbon has been completely burned off, the ash is cooled and weighed. If the ash is very large it may enclose carbon. This may be detected by moistening with alcohol, when any carbon which remains will show up, and may be readily burnt off.

(The importance of burning off gently at the beginning of the estimation may be explained by the fact that the coke which is formed when coal is gently coked is much more easily burnt off than the dense coke formed by quick coking, such as that obtained from the estimation of volatile carbonaceous matter.)

The calorific value of a coal is estimated by the complete combustion of a weighed quantity of powdered coal under such conditions that the quantity of heat generated can be measured. The most accurate way of doing this is by burning the coal in oxygen in a bomb specially constructed for the purpose. A Mahler calorimeter (Fig. 53) consists of a bomb B, made of toughened steel having a platinum or enamelled lining, a copper water bath D for same with stirrer S, and an outer bath A, also containing water, which is insulated outside by thick felt and from the inner bath by a light wood framework. The bomb has a cap which is screwed on with a strong thread and is made tight by means of a lead washer in a proper seating. The cap is fitted with two rods, made of platinum, one supporting the capsule C containing the coal, and the other, E, insulated from the cap, is used for firing the coal. The cap also contains a screw-down valve in the centre, for admitting oxygen, a sheet of mica just inside the cap protects the valve, and also serves to break up the current of gas. This valve is perhaps the weakest spot in the apparatus, as during the explosion any nitrogen present is oxidised to nitric anhydride, and the nitric acid thus formed attacks the metal of the seating and plug. This necessitated constant re-grinding, until the cause was discovered, when the simple expedient of running a few c.c. of standard sodium carbonate solution into the bomb, and swirling it round to moisten the walls, entirely overcame this difficulty. The sodium carbonate neutralises the acid formed, and incidentally allows

of a proper correction being made for the oxidation of nitrogen and sulphur, by titrating the amount of sodium carbonate left, and then calculating the heat of formation of the acids which have neutralised the known quantity of sodium carbonate.

The method of procedure is as follows: 1 gram. of the undried powdered coal is weighed, and transferred to the capsule which is supported from the cap. Four inches of thin iron wire (of which the weight is known) is taken, and its ends are twisted round the two rods in such a way as to form a loop which dips

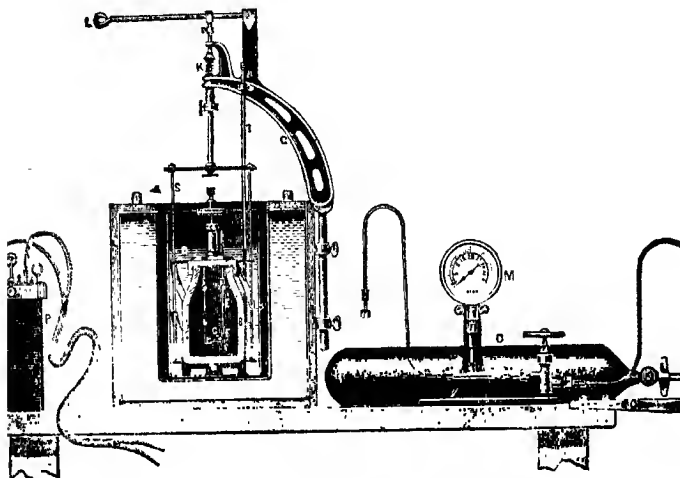


FIG. 53.—Mahler Bomb Calorimeter.

into the coal, and at the same time make a conductor between the two rods. Ten c.c. of $\frac{N}{2}$ sodium carbonate solution is run into the bomb, swirled round the walls, and the cap screwed on, care being taken that none of the coal is upset. The bomb is then filled with oxygen to 25 atmospheres, the valve is closed, and the whole immersed in the inner water bath, which has previously had 2 litres of water poured in. The bomb should be so gas-tight that no bubbles of gas escape. A thermometer, having a range of about 10° C., and graduated in $\frac{1}{100}$ of a degree and readable to 100° C., is immersed in the bath, and held in position by a clip provided for the purpose. The water is kept in motion by the stirrer until the temperature remains constant,

or, to save time, until the rise or fall is so regular that a correction can be applied. The temperature is recorded and the coal fired by passing a current, from an accumulator or some other suitable source, through the two rods, of sufficient energy to heat the iron wire to firing-point, which in turn ignites the coal. Whilst this is going on, the water should be stirred continuously, and the temperature noted at the end of thirty seconds, and the next thirty seconds, after that, every minute until it attains its maximum, and reaches a regular rate of falling. After corrections have been made for the regular cooling or heating of the apparatus, the difference between the temperature at the moment of firing and the highest temperature reached yields a figure which, when multiplied by the constant for the calorimeter, gives the number of calories evolved. From this the calories evolved by the oxidation of the iron, nitrogen and sulphur have to be deducted, the balance being the value of the coal in calories. If this is multiplied by 1.8 it will give value in terms of British Thermal Units, or, if divided by 536, in terms of water evaporative power, at 212° F. The constant varies with each calorimeter, and can either be calculated from the weights of the various materials used and their specific heats, or by direct determination of some material of definite calorific value, such as naphthalene.

This method is, however, unnecessarily elaborate for the ordinary routine of a works, and may only be required in cases of dispute. A much simpler calorimeter, which enables estimations to be made quickly and with sufficient accuracy for ordinary works use, is that devised by Roland Wild, and which is illustrated by Fig. 54. It consists of a combustion chamber with a screw cap and arrangement for firing a mixture of fuel and sodium peroxide, the whole of which is immersed in water contained in a copper bath, which in turn is enclosed in another vessel forming an air bath. The fuel is ignited by electrical means, or by dropping a piece of red-hot nickel on to the fuel through an aperture made for the purpose; the water is kept stirred and the rise of temperature noted. The quantity of water used is such as will bring the "constant" of the apparatus to 1000 for British Thermal Units, which simplifies the calculation. The thermometer is graduated to $\frac{1}{10}^{\circ}$ F., and can be read to $\frac{1}{20}^{\circ}$ or less. The rise in temperature in degrees F. multiplied by 1000 gives the value of the coal in British Thermal Units, and if this be divided by 965, the value in terms of

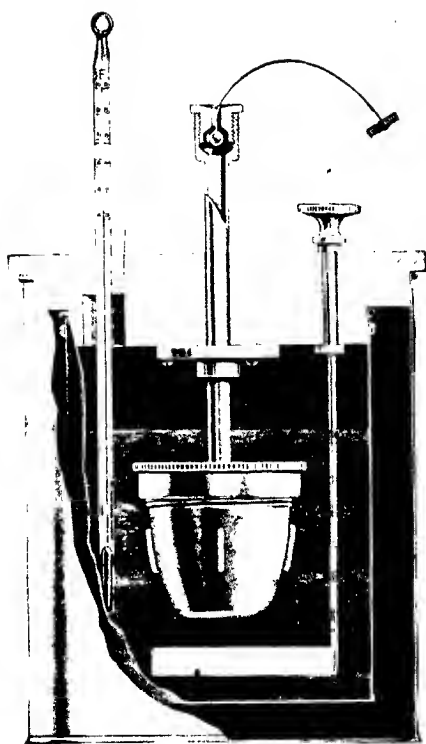


FIG. 51 —Roland Wild Calorimeter.

evaporative power of water at 212° F. will be obtained, or if divided by 1.8 it will give the value in gramme-degree calories.

Sulphur.—Should it be necessary to estimate the quantity of sulphur present, it can be done by a modified form of the Eschka method: 1 gm. of finely powdered coal is mixed with 1 gm. of magnesium oxide and 0.5 gm. sodium carbonate, transferred to a platinum crucible, and ignited over an alcohol or petrol burner—not gas—at first gently and then at a higher temperature, until all the carbon has been burnt off. This is greatly facilitated by stirring with a platinum wire. The residue is transferred to a beaker, and boiled for a few minutes with 15 to 20 c.c. saturated bromine water diluted to about 60 c.c. The solution is allowed to settle, the clear liquor filtered off, and the residue boiled again with water and filtered off into the same beaker. The combined filtrate is acidulated with a couple of c.c. of hydrochloric acid, boiled till all the bromine has been expelled, and 10 c.c. of barium chloride solution is added, the whole boiled for three to five minutes, and allowed to stand for a couple of hours, when the precipitate of barium sulphate may be filtered off, washed, dried, ignited, and weighed.

If the solution shows any sign of throwing down flakes of silica whilst boiling off the bromine, the solution should be transferred to a dish, evaporated to dryness, baked to render the silica insoluble, the residue digested with a little hydrochloric acid and water, filtered, and the filtrate treated with barium chloride as before. If the coal contains much pyrites or calcium sulphate there is a danger of leaving some of the sulphate in the magnesia residue. To remove this risk, the residue should be dissolved in hydrochloric acid, diluted, and tested with barium chloride.

Water.—It is sometimes necessary to examine the water in use on a cement works, especially if it has to be softened for boiler purposes. For this purpose little else is required beyond the total solids, hardness, alkalinity, and mineral analysis.

For total solids 50 or 100 c.c. of water is run into a weighed platinum dish, evaporated on a water bath, dried in an air oven at 105° C., cooled in a desiccator, and weighed. Owing to the hygroscopic nature of the residue, quick weighing is essential, and if necessary the solids are dried and weighed again.

Hardness is estimated by taking 50 c.c. of water (or if very hard, a smaller quantity is taken and diluted to 50 c.c.) in a

well-stoppered bottle of about 250 c.c. capacity, and adding standard soap solution by a c.c. at a time, followed by shaking, until the lather formed remains for five minutes without breaking down. The soap solution is so standardised that 1 c.c. is equivalent to 1 degree of hardness on 50 c.c. of solution taken. A test on distilled water should be made to find the quantity required to produce a permanent lather on pure water, and this amount (usually about 0.7 c.c.) should be subtracted from the figure obtained for ordinary waters.

There are various modifications of this process as to quantities, special methods for temporary and permanent hardness, and fine corrections for other irregularities which are detailed in textbooks devoted to this subject, but the method given above is sufficiently accurate for all ordinary purposes of "works control."

The alkalinity is estimated by titrating 500 c.c. of water with $\frac{N}{2}$ hydrochloric acid, using phenolphthalein as an indicator.

This is chiefly used for testing softened waters. Further titration of the same water with $\frac{N}{2}$ hydrochloric acid, using methyl orange as indicator, will give the amount of carbonate present. For the estimation of mineral constituents, 500 or 1000 c.c. of the water is evaporated to dryness with a little hydrochloric acid in a dish, covered, baked and analysed by the same method as described for cement in the chapter on "Methods of Analysis."

Oils.—The oil used for lubricating, etc., will need to be examined, but, generally speaking, all that is necessary is the determination of the specific gravity, viscosity, flashing point, and test for mineral acidity.

The specific gravity is usually determined by means of a specific-gravity bottle. This bottle has a drilled stopper, and the content, when filled to the top of the hole in the stopper, is calibrated by means of pure water at the temperature required, usually 60° F. The dry bottle is filled to the top with oil, cooled to the proper temperature, and the stopper forced in, the oil which overflows through the hole in the stopper being wiped off at once (any more oil which comes out because of expansion not being touched), and the bottle quickly wiped and weighed. The difference between this weight and the weight of the bottle is the weight of oil which occupies the known content of the bottle, and by dividing the weight of the oil by

that of the water content, the specific gravity of the oil is obtained.

Viscosity.—There are various types of viscometers or viscosimeters, all of which are purely arbitrary, and usually set against standard rape oil. The one in general use in this country at the present time is that devised by the late Sir Boverton Redwood

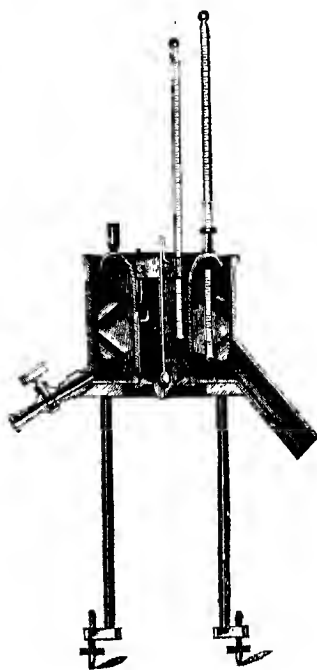
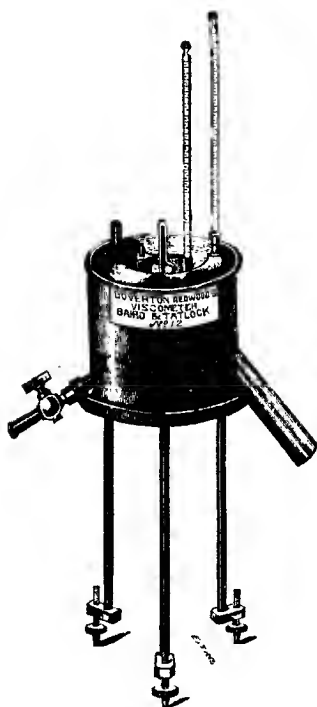


FIG. 55.—Redwood's Viscometer.

FIG. 56.—Redwood's Viscometer.

and illustrated in Figs. 55 and 56. The apparatus consists of an inner chamber, having a hole, of definite diameter and shape at the bottom which can be closed by means of a rod and ball, surrounded by a jacket forming a water or oil bath, which is fitted with a heating arrangement, stirrer, and a draw-off tap. In order that the hole in the inner vessel may remain of the same diameter, and also present as little friction as possible, it is drilled through a piece of agate. The bath is filled with oil or water, and when

heated to the proper temperature, the oil to be tested, previously heated to the required temperature, is poured into the inner vessel up to the ring on the wall, after the thermometer and closing valve are in position. When the oil has attained the correct temperature the valve is opened and the oil allowed to flow into a flask calibrated to hold 50 c.c., and the number of

seconds required to fill the flask to the mark is the viscosity figure. There are various fine adjustments to be made to this figure for very accurate work, but in the ordinary way only the actual seconds are stated. It is important that the inner vessel should be filled exactly to the mark, and that the temperature of the oil be maintained to within half a degree Fahrenheit through the determination.

Flashing-point.—This is also an arbitrary figure, and standard apparatus must be used for the purpose. The Pensky-Marten apparatus shown in Fig. 57 is used for oils having a flashing-point above 100° C. The Abel apparatus shown in Fig. 58 is used for light oils, and the apparatus without the water-bath, Fig. 59, is used on a sand-bath for heavier oils. The oil to be tested is poured into

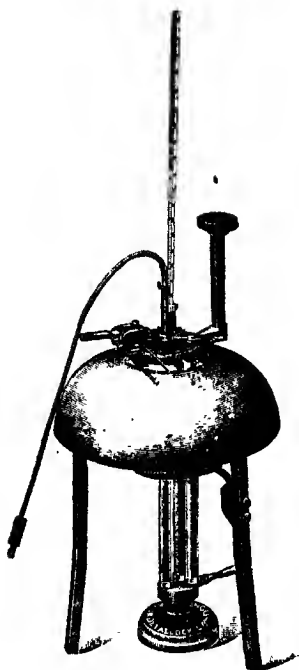


FIG. 57.—Pensky-Marten Flash-test Apparatus.

the inner vessel up to the mark, and the vessel closed, and heated up to about 20° below the flashing-point, when the gas is so adjusted that the increase is not more than 5° C. per minute. From time to time a small flame is placed at the mouth of the aperture, made by moving a slide in the lid, and when the space above the oil contains sufficient inflammable matter to "flash" the temperature (flashing-point) is noted.

Mineral Acid.—It is not often that free mineral acid is found in oils, but the test is so easily made that it is advisable to



FIG. 58.—Abel Flash-test Apparatus.

carry it out as a matter of routine when testing oils in order to detect any acid which might occasionally be present. All that is necessary is to put about 10 c.c. of oil in a test tube,

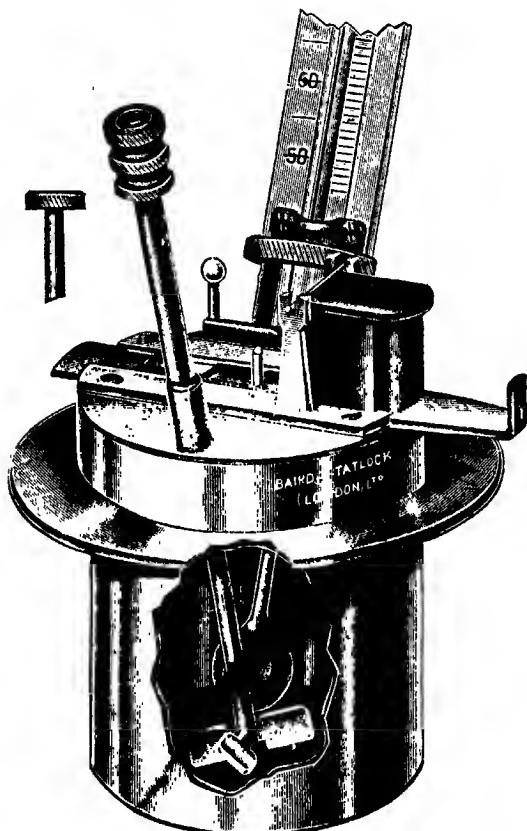


FIG. 59.—Abel Flash-test Apparatus. (Inner Vessel.)

shake it up with about an equal quantity of water, pour off the oil, and add a small drop of methyl orange solution to the aqueous extract. Any mineral acid present will colour the methyl orange pink.

CHAPTER · VII

TESTING

FROM the earliest days of the manufacture and use of Portland cement, it has been recognised not only to be essential but absolutely necessary that a strict control should be kept upon the quality of the cement before use. Many and varied are the tests which have been devised for the purpose, and while some of these have been really useful and remain in principle to the present day, many have fallen into disuse as their value has been proved to be a negligible quantity.

It was recognised quite early that the most important property of Portland cement was its strength; one of the earliest tests, introduced in 1830 by Major-General Pasley, R.E., with a view to determining the strength of mortars, consists of cementing bricks against a wall, one at a time, allowing the mortar to harden and cementing a second brick, and so on, to form a projecting beam. The cement which would carry the greatest number of bricks was taken as the best.

Vicat in 1828 devised his apparatus for determining the hardening of cement. The needle used for determining the setting-time, according to the British Standard Specification, is a modification of his original apparatus.

Very little real work was done in testing until 1858, when John Grant commenced a series of tests in connection with the construction of the London main drainage works. The present-day testing is mainly based on the principles established about this time, which consisted of tensile tests, tests for soundness and setting-time, fineness of grinding and weight per bushel.

Grant also carried out a good deal of experimental work in connection with the most suitable shape of the test-piece for tensile testing, and the most suitable clips for holding the briquette. The following extract is taken from a paper read by Mr. Grant before the Institution of Civil Engineers in 1880¹—

¹ *Proceedings Inst. of C. E.*, vol. lxii.

“Forms of Briquettes.”—For testing cement perhaps no point is of greater importance than the size and shape of the briquettes, and the kind of clips used in breaking them. As stated in his first paper, the author, in January 1859, adopted the form shown in Fig. 60, which had been in use for some years in France and England; but it was soon found to be capable of improvement, as the briquettes of this form broke with much irregularity. This was due partly to the imperfect shape, with sharp angles, and partly to the fact that the briquettes had to be pressed out of the moulds, which were in one piece, by a press devised and made by Mr. Adie. In the

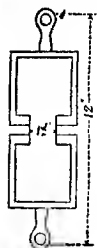


FIG. 60.—Early type of Clip.

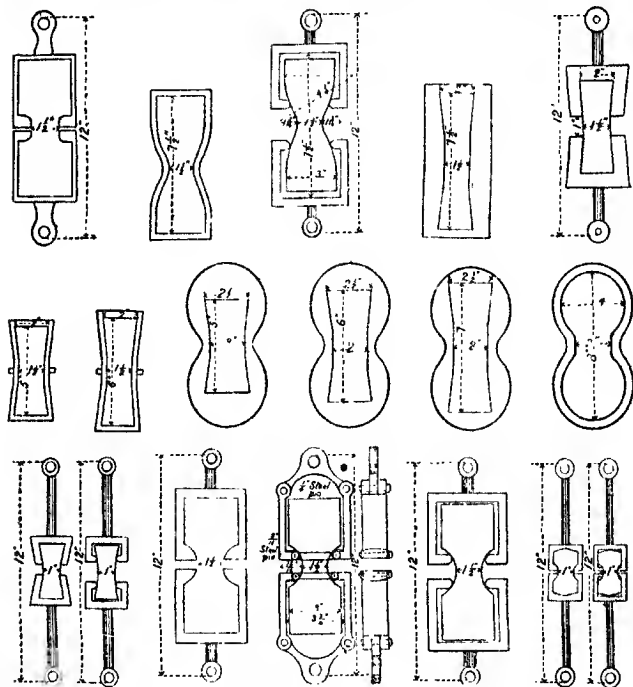


FIG. 61.—Types of Clips and Moulds. (Grant.)

process of removing them from the moulds, the briquettes occasionally got strained and cracked at the angles. these

imperfections not being always perceptible at the moment. The moulds were afterwards made to open in the middle and the small press was dispensed with. The form still seemed capable of improvement, and further experiments were made.

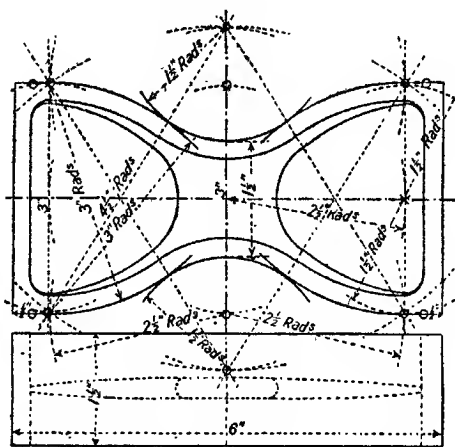


FIG. 62.—Form of Briquette adopted by Grant.

which will be best understood by reference to the type shown in Fig. 6I, which also shows various arrangements of the moulds intended to ensure accuracy, facility in use and economy of material. All tests have been

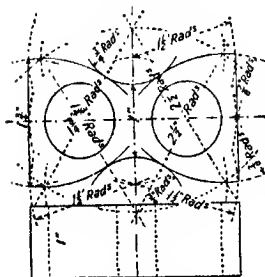


FIG. 63.—Form of Briquette adopted by Grant.

of material. All tests have been made since 1876-77 with briquettes of one or other of the two forms shown by Figs. 62 and 63. The fiddle-shaped form of briquette shown by Fig. 64 is that which has been adopted as the standard form in Germany. It has a breaking area of 5 square centimetres (2.25×2.22 centimetres). Being small, it is well adapted for making briquettes of




FIG. 64.



FIG. 64.

great density with very little trouble: but the shoulders seem too wide for the waist, and the little nick in the latter must have a tendency to produce cracks, and to make the briquettes

break prematurely. A briquette of 10 square centimetres area would be equal to 1.55 square inch. Since the author has used the small machine and the briquette of 1 square inch (Fig. 63), his confidence in the accuracy of both, even for experimental purposes, has increased. Some comparative experiments made with it and the larger briquettes of $1\frac{1}{2}$ in. \times $1\frac{1}{2}$ in. have been made, with the result that for testing cement the 1 inch briquette is as accurate as the other. The cement required to make one briquette of neat cement of the larger size ($1\frac{1}{2}$ in. \times $1\frac{1}{2}$ in., Fig. 62) will make five of the small (1 in. \times 1 in., Fig. 63).

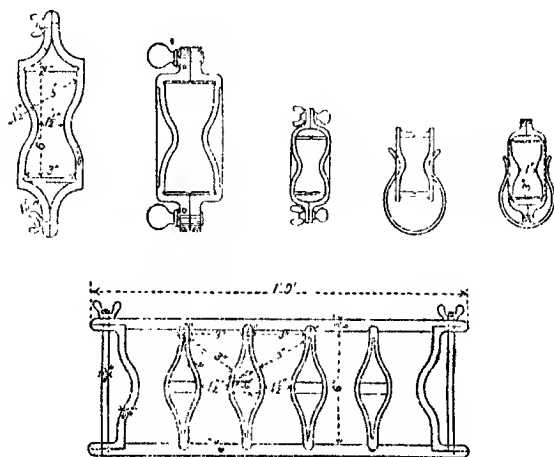


FIG. 65.—Various Types of Moulds.

"Moulds.—Some of the different kinds of moulds which have been used are shown by the above figures. Those now used are shown by Fig. 65. Comparative tests or experiments should be made with briquettes of the same size, shape and proportions.

"Clips.—Intimately connected with the shape of the briquette was the form of the clips by which they were held when being broken. For many years every attempt to improve them was in the direction of making them fit more exactly to the shape of the briquette, and, by means of knife edges, ball and socket joints and other contrivances, to get rid of all tendency to distortion; after numberless experiments the form shown on

Fig. 66 was found to be as nearly as possible free from error. The clips touch the briquette only at the lips, which are curved in both directions, and are, in fact, blunt, rounded points which allow of perfect freedom of action when the strain is applied. This form of clip has been used in every case with briquettes of the forms shown by Figs. 62 and 63.

"Effect of Improved Form of Briquette, Clip, etc.—The effect of the improvements in the mode of filling the moulds, in the form of briquettes, in the clips, and in the mode of testing, has been materially to increase the apparent strength of the cement tested. No doubt great improvement has been made in the manufacture of cement of late years. Still greater is certain yet to be effected;¹ but allowance must be made for the higher results now obtained by more accurate testing, when comparing the later with the earlier tests and requirements of engineers."

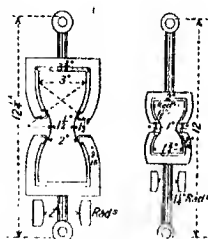


FIG. 66.—Form of Clips adopted by Grant.

A specification for the cement to be used on an important piece of work carried out in 1884 may be quoted as being an indication of what was regarded as the requirements of cement for a first-class job.

"The Portland cement must be of the best quality supplied by a firm to be approved by the engineer. It must be of good dark grey colour, uniformly burnt and finely and evenly ground; samples taken from different portions of the heap must show that it weighs on the average at least 116 lbs. per struck bushel in its dry, uncompressed state. Should a sample from any portion of the bulk submitted for test weigh less than 114 lbs. per struck bushel in its dry, uncompressed state, the whole parcel will be rejected. Sample test briquettes of a shape to be approved by the engineer, having a minimum section of $1\frac{1}{2}$ in. \times $1\frac{1}{2}$ in., must be made from the bulk of the cement after delivery on the works. They are to be placed in water 24 hours after gauging, and remain there until they are to be tested, and must bear at least the following tensile strains in one of Adie's testing-

¹ The accuracy of this prediction indicated Grant's full insight into the question.

machines fitted with the patent self-acting weight-traversing apparatus—

	Per block.
48 hours after gauging, inclusive of the 24 hours which the blocks are to be kept out of water .	350 lbs.
4 days	500 "
7 days	750 "

" The inspector will gauge the sample briquettes with so much water and in such a manner as he may think fit, and the briquettes are also to be broken by him. The contractor or his agent may be present at the time of gauging the sample briquettes and when they are subsequently tested.

" The inspector will also test pats made from the cement under trial, either by warming and watering them, or in any other manner which the engineer may deem necessary, with a view to determine whether the cement contains an excess of lime. He will likewise examine the fineness of the cement by taking samples from the bulk and passing them through a sieve having 2500 meshes to the square inch; in the event of more than 10% by weight of the samples being stopped by the sieve, the cement from which the said samples shall have been taken will be rejected and will not be allowed to be used in the works. The weight of the cement per bushel is to be ascertained by the inspector, who will slowly fill the measure through a hopper having an approved rectangular distributing shoot at the bottom of the same, the height or drop from the bottom of the hopper to the top of the bushel measure being 18 in., the cement to pass in thin films between the inside of the hopper and the outside faces of the distributing shoot. A drawing of the hopper will be furnished to the contractor by the engineer. The contractor is to provide the necessary testing-machine and such moulds, plates, water tank, hopper and other apparatus as the engineer may consider requisite for the convenient and efficient testing of the cement, all such testing apparatus to become the property of the authority and to be handed over to their representative on the completion of the contract in good order.

" No cement will be accepted which, having regard to the foregoing tests and conditions, is, in the opinion of the engineer, or inspector, too quick-setting, or that is over-limed and likely afterwards to fly in the work: neither will any cement be allowed to be used unless it complies with the above stipulations in all respects, and has been approved by the engineer or inspector.

"The cement is to be stored in bulk in the shed alluded to under the head of Temporary Works, Clause 33; each respective consignment is to be kept separate by timber partitions. The cement is to be emptied from the sacks directly it arrives on the works, and must be bulked and spread out so as not to be more than 3 ft. 6 in. in depth. It is to remain in store at least four weeks before being used, or longer if the engineer or inspector should so desire: during this time it shall be turned over once at least.

"The contractor shall provide all labour and cement necessary for making such tests as the engineer or inspector shall direct. Any cement which has been rejected or which may have been damaged by rain, damp or exposure, shall be removed at once from the works."

Specifications were drawn up by every engineer who had a piece of work to carry out, and with such different requirements that the manufacturers were often in great difficulties in endeavouring to comply. Occasionally, clauses were inserted which were contradictory in themselves. Many tests, too, have been devised as short cuts, such as the "Marmalade pot test," which had for its object the determination as to whether the cement contained any "free lime," and was therefore likely to be unstable. The test was to stir up a quantity of the sample with water in a pot, and insert a thermometer. If there was a rise in temperature beyond a certain limit, the cement contained "free lime," and was therefore unsound. This class of test, together with many others equally useless and unreliable, has been banished. The need for a standard specification applicable generally was long felt by all, users and manufacturers alike, but it was not until 1904 that the first British Standard Specification appeared. This was by no means an ideal specification, but may be regarded as a very fair attempt to meet the general conditions. It must be borne in mind that while many works could at this date comply with all requirements of the specification, there were many of the smaller works who were hard put to it to produce cement approaching these requirements, especially with regard to soundness and fineness.

A word may be said here with regard to the soundness test which was introduced into this specification. The test—*i. e.* the Chatelier test—met with much adverse criticism. The method, however, had been in use in the author's laboratory for a considerable period for comparison with the methods then recognised,

during which time it had proved itself to be not only a reliable test for detecting unsound cement but a test easy of manipulation, even in inexperienced hands, and, being a test based upon actual measurement, it is easier of interpretation than a doubtful pat. The following figures may be cited as an indication of the readiness with which the British manufacturers came into line with the specification. The figures are expressed in per cent. on the samples passing through the author's laboratory for examination.

Per cent. above British Standard Specification.

Before B. S. S.									
introduced	1903	31'5							
	1904	30'0	Expansion not to exceed	12'0	mm.				
	1905	17'7	"	"	"	"	"	"	"
	1906	15'8	"	"	"	"	"	"	"
To June	1907	15'7	"	"	"	"	"	"	"
" Dec.	1907	23'7	"	"	"	"	10'0	"	"
	1908	9'4	"	"	"	"	"	"	"
	1909	7'6	"	"	"	"	"	"	"
	1910	0'7	"	"	"	"	"	"	"
	1911	3'2	"	"	"	"	"	"	"
	1912	4'3	"	"	"	"	"	"	"
	1913	6'7	"	"	"	"	"	"	"
	1914	8'7	"	"	"	"	"	"	"

It will be convenient to take the tests as specified in the British Standard Specification and deal with them *seriatim*, the current British Standard Specification being the fourth issue and published in March 1915.¹

Test for Fineness

"The cement shall comply with the following conditions of fineness: 100 grms. of cement shall be continuously sifted for a period of 15 minutes on each of the under-mentioned sieves and in the order and succession given below, with the following results:—

- (1) The residue on the sieve, $180 \times 180 = 32,400$ meshes per square inch, shall not exceed 14 %.
- (2) The residue on a sieve, $76 \times 76 = 5,776$ meshes per square inch, shall not exceed 1 %.

The diameter of the wire for the 180×180 mesh sieve shall be .0018 in. and that for the 76×76 sieve, .0044 in. The wire cloth shall be woven (not twilled), the cloth being carefully mounted on frames without distortion."

¹ The abstracts from the British Standard Specification for Portland cement (Report No. 12, 1915) on this and subsequent pages are made by kind permission of the British Engineering Standards Association.

The 1904 specification allowed a residue of $22\frac{1}{2}\%$ on the 180×180 sieve and 3% on the 76×76 sieve, while the 1907 specification reduced the permissible residue to 18% on the 180×180 sieve, that on the 76×76 remaining the same. No alteration was made in the 1910 revision in respect of fineness.

In the days when the material as it left the burr stones was the finished product, the user had to be content with a material which left a residue approaching 25% on a 50×50 sieve, and at that date this was considered to be a very creditable performance as far as the manufacturer was concerned, and probably it was, considering the plant at his disposal. But when we take into consideration the function of the cement and consider the relation of the fineness of grinding to that function, it is evident that something better would be speedily required of the makers. Specifications were soon drawn up demanding finer grinding, and the manufacturer soon began to demand new devices for grinding. With the gradual introduction of good grinding machinery, the difficulties have been overcome and a much better product of much greater cementitious value is now to be obtained.

Speaking generally, the finer the material is ground, the greater its cementitious value. It is well known that the residue caught on the 76×76 sieve has no setting properties, and therefore it is desirable as far as possible that the whole of the cement should pass this sieve. The cementitious properties of the finished cement is very largely determined by the percentage of "flour" present.

Many attempts have been made to determine the "flour" in cement with more or less success, and as no method has as yet been standardised, nor any definition as to what shall be regarded as "flour," there is not much need to record here the many efforts. One reason which may account for the adhesion to the older and better-known methods of sieving is undoubtedly their simplicity of manipulation. The day may come when we shall be buying cement much as coal is bought in large quantities—that is, upon its actual value to the user (calorific value in the case of coal). Then we shall have a sliding scale according to the "cementitious value," based upon the percentage of sand the cement will hold together and give a certain tensile strain. Some such method appears to be the only rational basis of purchase. Of course, other tests would be applied to cement to determine its suitability or otherwise for a particular piece of work.

Test for Specific Gravity

The British Standard Specification requires that—

“The specific gravity of the cement when presented by the manufacturers for testing shall be not less than 3.10.”

Various methods have been devised to facilitate the determination of the specific gravity of cement. There is no need to go into these in detail; the one most recently devised, and recommended by the Standard Committee (see Fig. 67), is easy to handle, and requires a single piece of apparatus only. It consists of a flask, the bottom bulb of which shall hold not less than 100 c.c., with a short scale which can be read off to give the zero. The neck of the flask carries a bulb and the neck is graduated from the zero so that the exact volume of the known weight of cement added can be measured.

The method is as follows:—A sufficient quantity of previously dried paraffin oil or turpentine is filled into the flask in such a manner that the bulb and neck are not “wetted.” The flask is then immersed in a water bath, preferably at the laboratory temperature, and allowed to become constant in temperature,

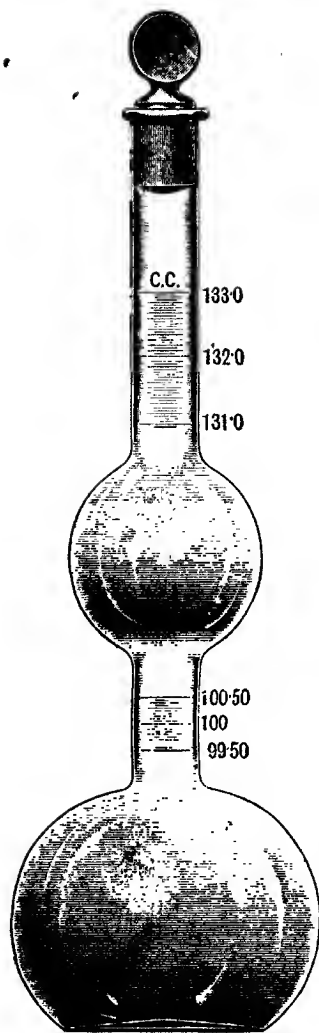


FIG. 67.—Specific Gravity Flask.

the temperature being noted. The volume is now accurately read off and noted, there being no need for the volume to be at

zero, addition or subtraction being made to the final reading; 100 grammes of the sample are now filled into the flask by means of a short-stemmed funnel. The whole is shaken to eliminate air bubbles, then placed again into the water bath and brought back to the original temperature, the volume read off, and the necessary corrections made. Divide the weight of cement taken by the volume, and the result is the specific gravity.

Tensile Strength (Neat Cement)

The British Standard Specification requires that—

“The breaking-strength of neat cement shall be ascertained from briquettes of the shape shown in Fig. 68.

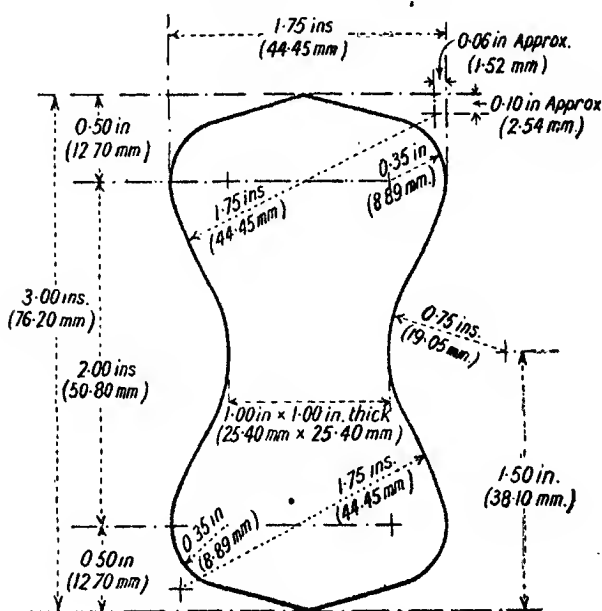


FIG. 68.—Standard Briquette. (Dimensions.)

“The briquettes shall be prepared in the following manner—

“The cement shall be mixed with such a proportion of water that the mixture shall be plastic when filled into the moulds used for forming the briquettes.

“The cement, gauged as above, shall be filled into moulds of

the form required to produce briquettes of the shape shown in Fig. 68, each mould resting upon a non-porous plate. In filling the moulds the operator's hands and the blade of the ordinary gauging trowel should alone be used. The trowel should weigh about $7\frac{1}{2}$ ozs. No ramming or hammering in any form will be permitted, nor shall any other instrument or apparatus other than the trowel before described be employed for this operation. The moulds after being filled may be shaken to the extent necessary for expelling the air.

"Clean appliances shall be used for gauging, and the temperature of the water and that of the test-room at the time that the above operations are being performed shall be from 58° F. to 64° F.

"The briquettes shall be kept in a damp atmosphere for 24 hours after gauging, when they shall be removed from the moulds and immediately submerged in clean water and left there until taken out for breaking. After they have been so taken out and until they are broken, the briquettes shall not be allowed to become dry. The water in which they are submerged shall be renewed every 7 days and shall be maintained at a temperature of between 58° F. and 64° F.

"The briquettes shall be tested for breaking-strength at 7 and 28 days respectively after gauging, 6 briquettes for each period. The breaking-strength shall be the average tensile breaking-strength of the 6 briquettes for each period. The briquettes to be tested shall be held in strong metal jaws of the shape shown in Fig. 69, and the load shall be steadily and uniformly applied, starting from zero, and increased at the rate of 100 lbs. per square inch of section in 12 seconds.

"The breaking-strength of the briquettes at 7 days after gauging shall be not less than 450 lbs. per square inch of section.

"The breaking-strength of the briquettes at 28 days after gauging shall show an increase on the breaking-strength at 7 days, and shall be not less than the number of pounds per square inch of section, arrived at from the following formula—

"Breaking-strength at 7 days + $\frac{40,000 \text{ lbs.}}{\text{breaking strength at 7 days.}}$ "

This is an advance on the previous specification in that the 7 days' test shall be not less than 450 lbs. per square inch instead of 400 lbs. It is an unusual occurrence for a cement of modern manufacture to give less than 450 lbs. per square inch, and

therefore no difficulty is experienced in complying with the requirements.

Another advance in this specification is the introduction of a formula for the increase of strength between the 7 days and the 28 days, in place of the old scale of varying percentage increase according to the 7 days' breaking-strain.

The gauging of cement and the filling into the moulds are operations calling for considerable skill and experience. There

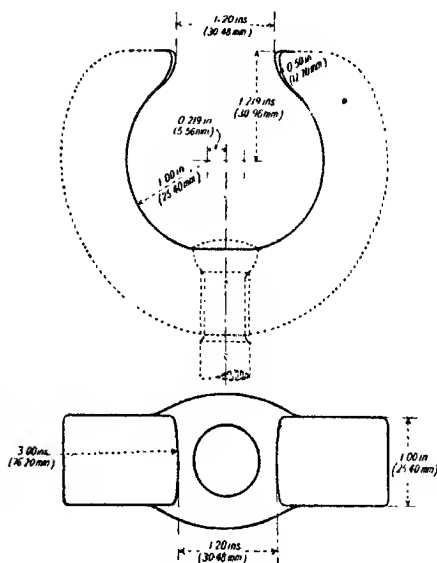


FIG. 69.—Standard Jaws. (Dimensions.)

is still the mistaken idea that any one can control the supply of cement coming on to the job, and this duty is often relegated to the clerk of the works, already overburdened with other duties, to carry out in his spare time. The result is either a good deal of friction with the manufacturers, or else the cement gets in without any supervision whatever—both are very undesirable proceedings, especially the latter, because if a consignment of cement should be used and afterwards proves to be unsuitable, a large amount of avoidable trouble and expenditure of both money and material will have been made. This applies not only to the

neat tests but to all tests, and it cannot be too strongly emphasised that each test in the specification has been devised with the object of controlling some particular chemical or mechanical property of the cement, and that a satisfactory estimate of the value of the material cannot be made without complete tests.

Tensile Strength (Cement and Sand)

The British Standard Specification states that—

“The breaking-strength of cement and sand shall be ascertained from briquettes, also of the shape shown (Fig. 68). The briquettes shall be prepared in the following manner—

“A mixture of cement and sand in the proportion of one part by weight of cement to three parts by weight of the standard sand specified on p. 148 shall be gauged with sufficient water to wet the whole mass throughout without any excess of water being present.

“The mixture, gauged as above, shall be evenly distributed in moulds of the form required to produce briquettes of the shape shown in Fig. 68, each mould resting upon a non-porous plate. After filling a mould a small heap of the mixture shall be placed upon that in the mould and patted down with the standard spatula shown in Fig. 70 until the mixture is level with the top of the mould. This last operation shall be repeated a second time and the mixture patted down until the water appears on the surface; the flat only of the standard spatula is to be used, and no other instrument or apparatus is to be employed for this operation. The mould after being filled may be shaken to the extent necessary for expelling the air. No ramming or hammering in any form will be permitted during the preparation of the briquettes, which shall then be finished off in the moulds by smoothing the surface with the blade of a trowel.

“Clean appliances shall be employed for gauging, and the temperature of the water and that of the test-room at the time the above operations are performed shall be from 58° F. to 64° F.

“The briquettes shall be kept in a damp atmosphere for 24 hours after gauging, when they shall be removed from the moulds and immediately submerged in clean fresh water, and left there until taken out for breaking. After they have been so taken out and until they are broken the briquettes shall not be allowed to become dry. The water in which they are submerged shall

be renewed every 7 days and maintained at a temperature of between 58° F. and 64° F.

"The briquettes shall be tested for breaking-strength at 7 and 28 days respectively after gauging, 6 briquettes for each period. The breaking-strength shall be the average tensile breaking-strength of the 6 briquettes for each period. The briquettes

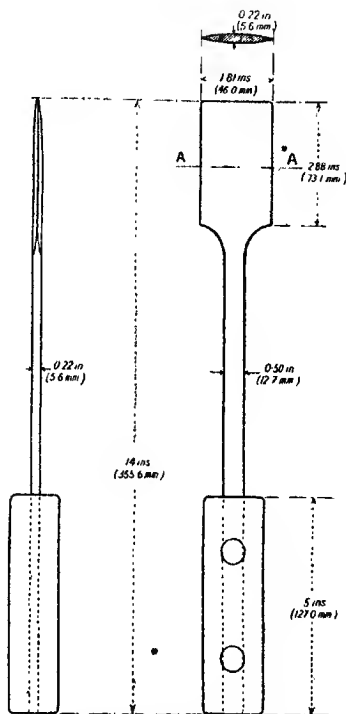


FIG. 70.—Standard Spatula.

to be tested shall be held in strong metal jaws of the shape shown in Fig. 69, and the load steadily and uniformly applied, starting from zero, and increased at the rate of 100 lbs. per square inch of section in 12 seconds.

"The breaking-strength of the briquettes at 7 days after gauging shall be not less than 200 lbs. per square inch of section.

"The breaking-strength of the briquettes at 28 days after

gauging shall show an increase on the average breaking-strength at 7 days, and shall be not less than the number of pounds per square inch of section arrived at from the following formula—

$$\text{" Breaking-strength at 7 days + } \frac{10,000 \text{ lbs.}}{\text{breaking-strength at 7 days.}}$$

" The standard sand shall be obtained from Leighton Buzzard, be thoroughly washed and dried, and shall pass through a sieve of 20×20 meshes per square inch, and be retained on a sieve of 30×30 meshes per square inch. The sieves shall be prepared from wire-cloth, the wires being .0164 in. and .0108 in. in diameter respectively. The wire-cloth shall be woven (not twilled), the cloth being carefully mounted on the frames without distortion."

The tensile strain required at 7 days in each of the previous specifications was not less than 150 lbs. per square inch. This is now increased to 200 lbs per square inch, and cannot be regarded as too stringent, as the majority of the manufacturers would claim that the whole of their output would not be below 250 lbs.

As in the case of the neat cement, a formula has been introduced for calculating the required increase in strength between the 7 days and the 28 days.

A good deal of difficulty has been caused between users and manufacturers in regard to the methods of filling the moulds. The statement " shall be filled, without mechanical ramming," being somewhat vague, a long-felt want has been supplied by the introduction of the Standard Spatula. There is a good deal to be said for and against standardisation, but when some manufacturers were using only " thumb pressure," some the Böhme Hammer apparatus, and others the Spatula, it was impossible for any one testing cement to get results in any sort of agreement.

Widely differing results can be obtained by using different percentages of water, and as the cement, according to its quality, will require more or less water, it is not advisable to state a definite percentage of water to be used in gauging.

A good deal of work has been done in the way of tensile testing-machines, and, as is often the case, the most simple contrivance is the best.

The simplest form of machine is that designed by Messrs. Patrick Adie many years ago. It consists of a single lever steel-yard, with an arrangement to increase the load automatically.

The machine is shown in Fig. 71. A brief description of the apparatus will serve to show its many good points, not the least being its simplicity. The lever *F* is supported by a knife edge resting in a bearing on the top of the main pillar *A*. The briquette is held by clips *B* and *C*, both of which are fitted with ball-and-socket joints, the clip *B* being hung from *F* by a knife

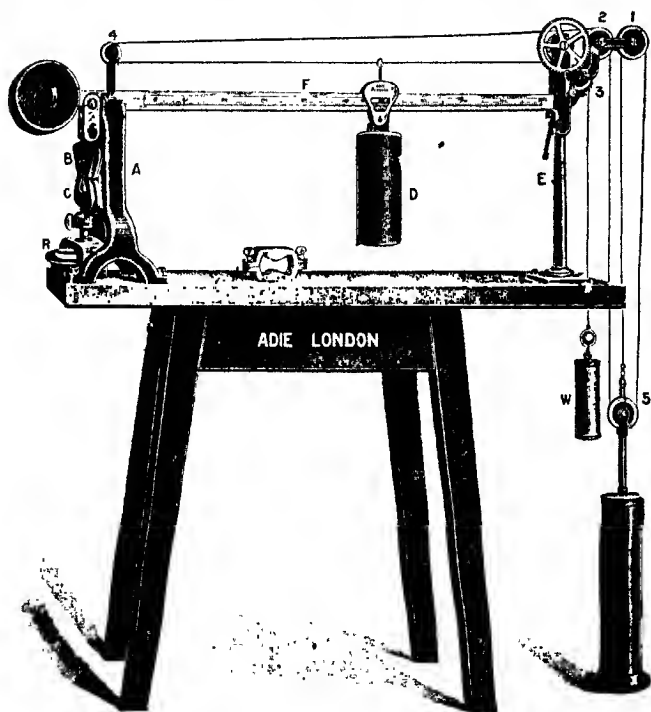


FIG. 71.—Adie's Testing Machine.

edge, whilst clip *C* is adjusted by means of the screw and wheel *R*. A sliding weight *D* moving slowly along the graduated lever *F* causes a smooth and regular increase of the tension on the briquette until the breaking-point of the latter is reached. The rest of the machine is for the purpose of making the movement of the weight *D* completely automatic. A flexible wire, one end of which is attached to the piston of the dashpot, after passing over pulleys 1, 5, 2, and 4, is connected to the top of the weight

D and then passes round pulley 3 twice, and terminates in a weighted hook from which is hung the weight W. There is also a stop attached to pulley 3 which is operated by a trip worked by the lever F, afterwards released by a lever cam E lifting F. The action is as follows. The weight D starting from zero (*i. e.* close to A) is pulled along the lever F, by means of the weight W, and the speed of this movement is regulated by the dashpot which is adjusted to allow an increase of 100 lbs. in twelve seconds, the speed stated in the British Standard Specification. As soon

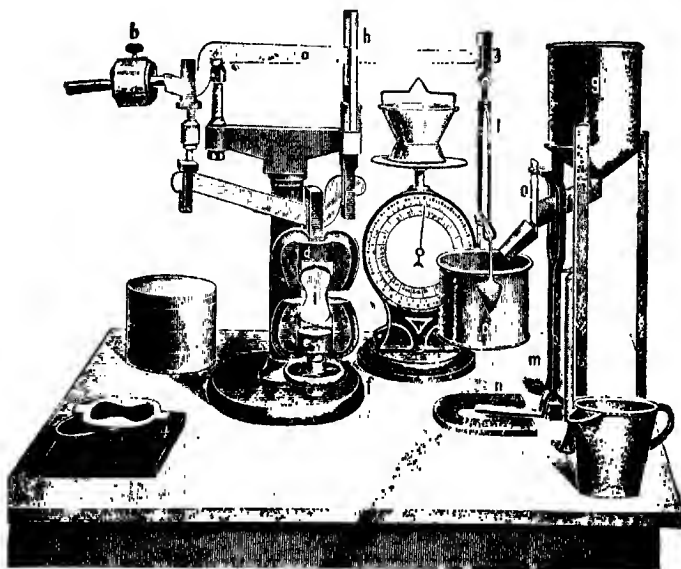


FIG. 72.—Shot Machine.

as the briquette breaks, the lever F falls, and causes the trip to stop any further movement of the weight.

A form of machine in use on the Continent is the multiple lever, and commonly referred to as the Shot Machine shown in Fig. 72. The levers are so arranged that there is a ratio of 50 to 1 between the load applied and that exerted on the test-piece. The main lever *a* is supported by means of a knife edge, and is free to move up and down through the guide *h*. A bucket *c* is suspended from one end of the lever and a counter-weight from the other, both being supported on knife edges. This lever is con-

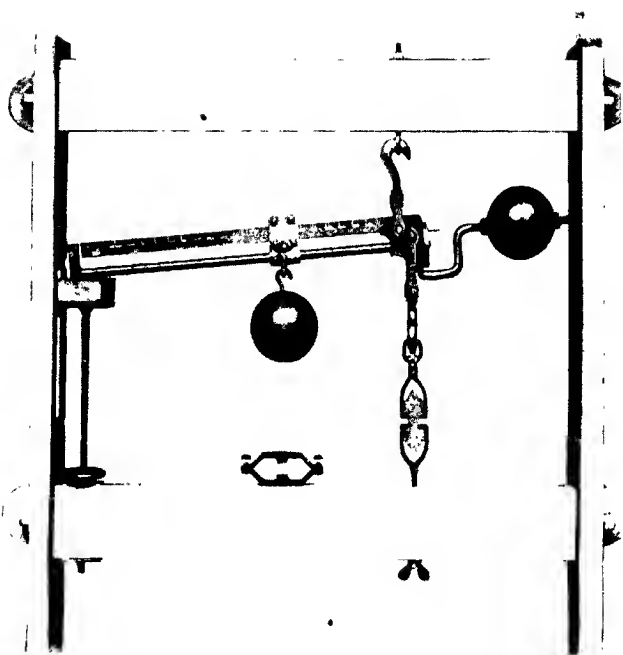


FIG 73 —Early type of Tensile Machine.

connected with a second lever, which is connected with the clip *d*, the briquette *i* being held between this and the lower clip *e*. The load is applied in the following manner:—shot, contained in the hopper *g* and regulated by the slide *o*, is run into the bucket at the standard rate until the briquette breaks. As soon as this happens, the bucket falls on to the trip *n*, which, through the connecting rod *m*, closes the slide *o*, and so automatically stops the flow of shot. The bucket is transferred to the spring balance and the weight read off. Many other forms have been devised, the two mentioned being those in general use. It may be of interest to show one of the earliest forms of machine (Fig. 73). This machine was designed for testing briquettes of $1\frac{1}{2}$ in. \times $1\frac{1}{2}$ in. section of the form described by Grant in his earliest work (see p. 135). The briquette having been placed in position, the load is taken up by means of a screw, and the load applied by means of the weight, which is moved along the steelyard by the screw, which is controlled by turning the small wheel immediately above the jaws. I have to thank Messrs. Cubitt for the use of this illustration.

Tests for Setting-time

The British Standard Specification states that—

“ Unless a specially slow setting cement be required of which the minimum time of setting has been specified, the cement shall be of one of three distinct gradations of time of setting, designated as ‘ Quick,’ ‘ Medium,’ and ‘ Slow.’

“ Quick.—Initial setting-time not less than two minutes.

Final setting-time not less than ten minutes, nor more than thirty minutes.

“ Medium.—Initial setting-time not less than ten minutes.

Final setting-time not less than thirty minutes, nor more than three hours.

“ Slow.—Initial setting-time not less than thirty minutes.

Final setting-time not less than three hours, nor more than seven hours.

“ The initial and final setting-times of the cement shall be determined by means of the Vicat needle apparatus shown in Fig. 74.

“ For the purpose of carrying out the tests, a test-block shall be made as follows—

“ Neat cement shall be gauged in the manner and under the

conditions referred to in Clause *ix*, and the gauging shall be completed before signs of setting occur. The test-block shall then be made by filling the cement gauged as above into the Vicat mould, the mould resting upon a non-porous plate. The mould shall be completely filled, and the surface of the test-block shall then be smoothed off level with the top of the mould.

"For the determination of the initial setting-time the test-block confined in the mould and resting on the plate shall be placed under the rod bearing the needle, when the latter shall then be lowered gently into contact with the surface of the test-block and quickly released, and allowed to sink into the same.¹ This process shall be repeated until the needle, when brought into contact with the test-block and released as above described, does not pierce it completely. The period elapsing between the time when the cement is filled into the mould and the time at which the needle ceases to pierce the test-block completely shall be the initial setting-time above referred to.

"For the determination of the final setting-time the needle C of the Vicat apparatus shall be replaced by the needle F, shown separately on Fig. 74. The cement shall be considered as finally set when, upon applying the needle gently to the surface of the test-block, the needle makes an impression thereon, while the attachment shown in the figure fails to do so. In the event of a scum forming on the surface of the test-block, the underside of the test-block may be used for determining the final set."

Widely differing results were obtained, until the methods and conditions were specified. No property of Portland cement is more affected by outside influence than is the setting-time.

The temperature of the cement, the gauging water, and the air of the testing-room play a very important part in the rate of setting. It is therefore of the utmost importance that the whole of the materials to be used during the operations should be brought to the same temperature, and as the results generally required are for comparative purposes, the figures will be in very fair agreement if the work is carried out at the temperatures specified

¹ The Vicat needle may, if desired, be fitted with a mechanical attachment such as a "dashpot," so as to ensure the steady and gentle application of the point of the needle to the surface of the test-block, and thereby render the test independent of the hand of the operator. Care must be taken that the needle rests with its full weight upon the surface of the test-block.

by the British Standard Committee, viz. between 58° F. and 64° F.

The percentage of water used also has a marked effect upon the rate of setting, and as this largely has to depend upon the discretion of the operator, it is not so readily standardised as the temperature.

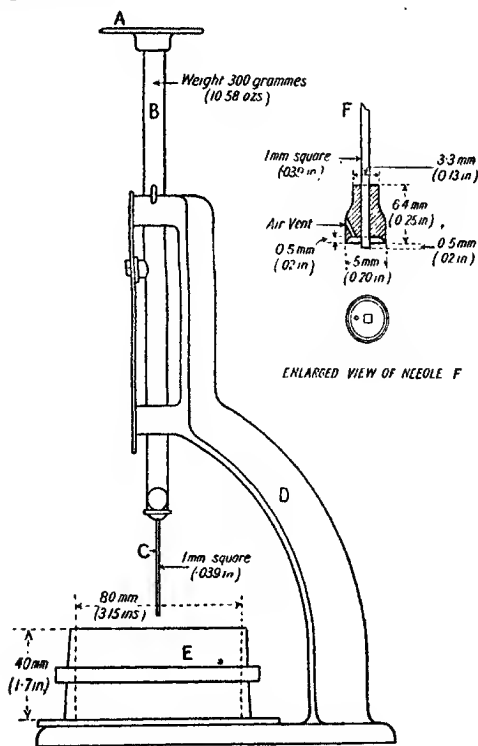


FIG. 74.—Vicat Needle Apparatus.

The following table gives typical results obtained with varying percentages of water. In each case the lowest percentage of water used is that required by the British Standard Specification, and would be used normally in testing; the highest percentage used being that required to give normal consistency. The Vicat needle was used in all cases to determine both the initial and final sets.

	% Water Used	Initial Set. Min.	Final Set. Min.
Cement No. 1 . . . {	21½ 24½ 27	15 20 30	75 90 120
Cement No. 2 . . . {	22½ 25 27	25 60 85	75 190 220
Cement No. 3 . . . {	22 24½ 27	30 85 135	140 190 285
Cement No. 4 . . . {	22½ 25 27½	15 30 95	65 120 230
Cement No. 5 . . . {	22½ 25 27½	13 25 30	100 180 210
Cement No. 6 . . . {	22½ 25 27	12 15 15	145 220 305
Cement No. 7 . . . {	22½ 25 27½	20 120 190	165 340 440
Cement No. 8 . . . {	22½ 25 27½	20 40 80	60 135 225
Cement No. 9 . . . {	24 27 31	30 85 100	120 255 300

It will be seen that the tendency is to prolong the setting when an excess of water is used, and emphasises the need for all work to be done as far as possible under definite conditions.

Soundness, Constancy of Volume

The British Standard Specification requires that—

“The cement shall be tested for soundness by the Le Chatelier method. The apparatus for conducting the Le Chatelier test

is shown on Fig. 75. The moulds shall be kept in good condition, having the jaws not more than 0.5 mm. apart.

"In conducting the test the mould shall be placed upon a small piece of glass and filled with cement gauged in the manner and under the conditions referred to on p. 143, which see. The mould shall then be covered with another glass plate, upon which a small weight shall be placed, and the whole shall then be immediately submerged in water at a temperature of 58° F. to 64° F., and left there for 24 hours. The glass plates are then removed and the distance separating the indicator points measured. The mould is again submerged in water at 58° F. to 64° F., which shall be brought to boiling-point in 25 to 30 minutes and kept boiling for 6 hours. The mould shall then be removed from the water and allowed to cool,

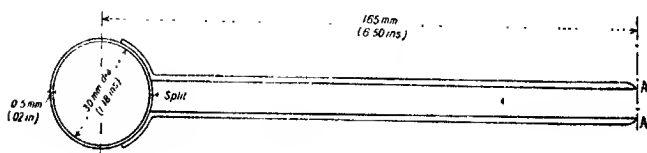


FIG. 75.—Le Chatelier Apparatus.

and the distance between the points again measured; the difference between the two measurements represents the expansion of the cement. When the sample has been aerated for 24 hours in the manner described, the expansion as above determined shall not exceed 10 mm. In the event of the cement failing to comply with this test, a further test shall be made from another portion of the same sample after it shall have been aerated for a total period of 7 days in the manner before described, when the expansion determined as above shall not exceed 5 mm."

The British Standard Specification requires that before the samples are submitted to the tests for tensile strength, setting-time and soundness, they shall be aerated for 24 hours, at a depth of 3 inches, the temperature being maintained between 58° F. and 64° F.

The least that can be expected of Portland cement is that it shall remain stable and sound after having been used for its legitimate purpose as a binding material. The tests for constancy of volume are of a fair and simple character, and although

a great deal of good and useful work has been done with cement which has been passed on a cold water pat, it has been generally accepted that an accelerated test is the only rational one. A defect which would only be indicated by a month of delay during exposure to cold water, would in most cases be shown up in an hour or so in boiling water.

The original method for testing soundness of cement was to gauge a pat of neat cement, about 3 in. in diameter, the centre being about $\frac{3}{8}$ in. thick and with tapering edges. This was allowed to remain for 24 hours in a moist atmosphere, and was

then placed in cold water and kept for 28 days. No signs of cracking or warping should appear in a sound cement.

A method which was regarded as a great advance on the cold pat was that introduced by the late Henry Faija. A pat of neat cement was prepared and immediately placed in the steam space provided in the top of a specially arranged bath (Fig. 76). The pat, after 5 or 6 hours in the steam, was lowered into the water below kept at a temperature of 115° F.—120° F. for the remainder of the 24 hours. At its date the test had its worth. The pat should remain firm on the plate

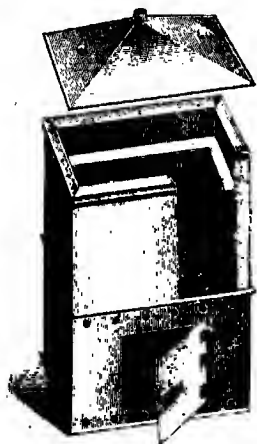


FIG. 76.—Faija Bath.

and show no signs of warping, cracking or shrinkage.

A further advance in accelerated tests was that of M. Deval. Pats were prepared as before described, and allowed to set in moist air for 24 hours, and were then immersed in a water bath the temperature of which was kept constant by a specially constructed bath (Fig. 77), at a temperature of 176° F. The bath consisted of a small copper tank A, provided with a cover I and surrounded by an outer jacket C, an air space D being provided between the two baths, the outer jacket being kept boiling. The temperature of the inner bath is adjusted by partially filling the air space with sand, E, and once adjusted the temperature remains constant. The outer bath is provided with

a condenser F, so that very little attention is necessary. This bath was also used for accelerated tensile tests. Briquettes prepared in the usual way were subjected to the hot water and broken after periods of 3 days and 7 days, the idea being that the results would be comparable with the 7 days' and 28 days' cold-water test. While there is no direct ratio between the hot and cold tests, it can be accepted generally that a cement which develops a good increase in strength between the 3 days and 7 days in the hot-water test will also show a good increase in the cold-water test.

Other tests for soundness have been devised, such as that of filling a glass bottle or a test-tube with the plastic cement, these being put aside to set. If at the end of 7 days the vessel had

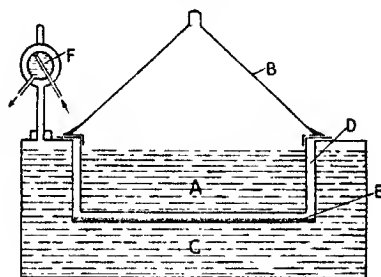


FIG. 77.—Deval Bath.

cracked, the cement was regarded as unsound, and probably rejected, no allowance having been made for the different coefficient of expansion of glass and cement.

Among the erroneous tests is the plunge test. A pat was prepared and immediately on gauging was immersed in water, the pat to show no signs of cracking or warping. The least that can be said is that such a test is without value as a guide to the soundness, and while a quick-setting cement, sound or otherwise, may give a good pat under those conditions, the reverse will happen with a slow-setting cement. Also, if several pats are prepared from the same cement under precisely similar conditions, the resultant pats will show all stages of apparent unsoundness.

A well-designed apparatus for actually determining the expansion or contraction of cement is that devised by the late Prof.

Bauschinger and shown in Fig. 78. It consists of a form of micrometer, and is designed to measure a bar of cement approximately 100 mm. long; movements of ± 0.01 mm. can be determined.

The apparatus is constructed of brass, and the micrometer frame is counterbalanced so that there is no undue strain on the points. The bar is provided with end plates punched with a centre point, so that the measurements are always taken from the same point.

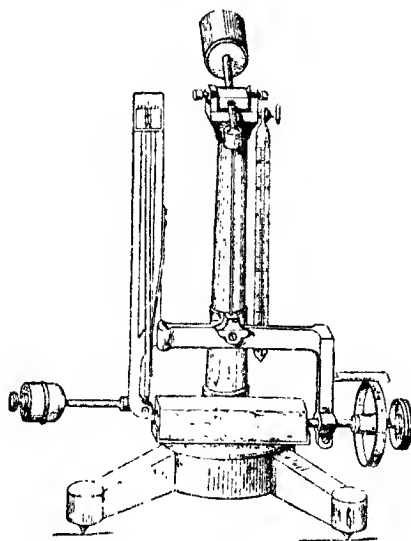


FIG. 78.—Bauschinger Apparatus.

The bar to be measured is placed in position on the platform provided, the micrometer points brought into position and the micrometer screw tightened in order that the same pressure shall be exerted every time; the left-hand point is provided with a pointer, the final adjustment being made when the pointer coincides with the central division on the scale. It is important that the instrument should be kept at a fairly constant temperature, and the temperature recorded at the time of reading. Standardised bars of cement and wood are provided for the purpose of correction, the length of the bars at 15° C. being

stated as data. The results are good, but the method is too cumbersome for ordinary use.

Compression tests, although fairly common in continental specifications, are not often specified in this country. It is generally argued that cement is more often used in compression than tension, and there is a good deal to be said on this point. It is often desirable to know the compressional strength of concrete, and there is no doubt that, if a series of experiments were

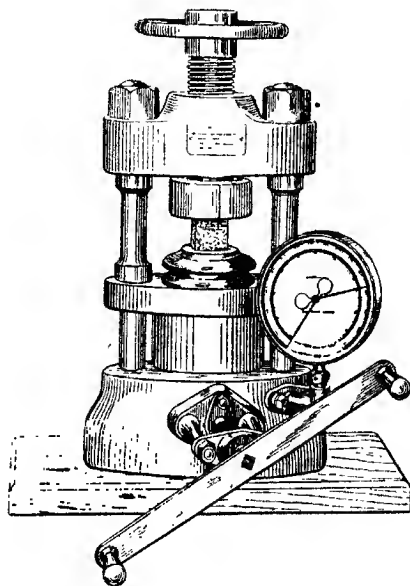


FIG. 79.—Compression Machine.

made before drawing up a specification as to the proportion of cement to aggregate to be used in a particular piece of work, a good deal of expense could be saved by reducing the cement used, still leaving a sufficient factor of safety.

In carrying out the test either neat or with standard sand, concordant results can be obtained by using 3 in. cubes, but for testing concrete it is advisable to make 6 in. cubes, or, if possible, 12 in. cubes. One of the chief reasons for the compression test not being specified is that it is costly. The tensile test is comparatively simple and cheap. The compression test requires a

somewhat expensive machine for crushing the cubes, but when the engineers of this country really take up the scientific testing of their materials, there is no doubt that this objection will disappear, as they will realise fully that it will pay in the long run.

A useful compact machine for carrying out the compression test is that shown in Fig. 79, and is manufactured by the Associated Portland Cement Manufacturers, Ltd. It is designed to test cubes up to three inches, and will give a maximum load of fifty tons.

CHAPTER VIII

METHODS OF ANALYSIS

Chemical Analysis

UNDER the heading of "Works Control" the various analytical methods used for maintaining control are fully described. These methods, although rather rough, are sufficiently accurate for the purpose in view, and the law of "constant error" may come into full play without detriment—*c. g.* a calcimeter may have a constant error, but it matters little whether the reading be high or low so long as it is consistent—*i. e.* with any particular reading, one can be sure of obtaining the same result. Sometimes, however, it is necessary to make analyses with a greater degree of accuracy, and the methods described in this chapter, if carefully carried out, will give results sufficiently accurate for all purposes.

It is not claimed that these methods are the only ones suitable, or that, in expert hands, many short cuts might not be introduced, but the object has been to describe reliable methods which could be carried out by any ordinary chemist, as distinct from the expert. The investigation of a new cement project is a typical case where reasonable accuracy is necessary, as slipshod methods may cause a good proposition to be turned down, or, on the other hand, may be the means of causing a great deal of trouble by allowing unsatisfactory materials to slip through.

Sampling

The importance of proper sampling has been emphasised in connection with the "works control," but it is still more important that the material on which a cement proposition is to be based should be properly sampled. For example, a limestone may be practically pure with the exception of siliceous veins running through it. If the sample is taken carelessly, it may contain far too large a proportion of the siliceous material, or, on the other hand, it may be a picked sample, containing nothing but practically pure limestone. In either case the result will be misleading.

A more common error in sampling new raw materials for cement making is to take the superficial material. If a new property is being inspected it is not an easy matter to obtain a sample representative of the bulk. Nevertheless this must be done, and the top layers or "overburden" must be removed before a proper sample can be obtained. After this has been done, the sample should be carefully selected to get the proper proportion of veins and other irregularities included, but pieces of "weathered" rock should be rejected, as it may have altered considerably in composition, and not be representative of the bulk. It is also advisable to take as large a sample as possible. The "average" from a few hundredweight is far more likely to be representative of the bulk than that taken from a few pounds, but even the latter is better than the sample which is sometimes taken by people who have not realised the importance of proper sampling—for example, a piece of weathered stone weighing about half a pound. There is a similar difficulty with sampling the other materials—*e. g.* clays may have pockets or patches of sandy matter or silt, which must be taken in their proper proportion if the results are to be of any use.

More might be written on this subject; but sufficient has been said to show that it is of the utmost importance that the sampling shall be thoroughly and intelligently carried out, and that there are many difficulties to be overcome before this can be accomplished.

The primary calcareous materials—chalk and limestone—are analysed as follows—

A preliminary examination is made by treating a small quantity of the material with hydrochloric acid to see if it is siliceous, argillaceous, dolomitic, etc., and examining the residue qualitatively, as the method of opening up has to be modified if there is much insoluble residue left.

If the material is nearly pure, or only dolomitic, 0.5 gm. of the finely-ground sample is weighed out, placed in a shallow porcelain dish about 6 in. in diameter, and swirled round with a little water until thoroughly mixed. The dish is covered with a watch-glass, about 20 c.c. of hydrochloric acid (sp. gr. 1.15) added, a little at a time to prevent loss by spurting, and the whole kept gently shaken until effervescence has ceased. The whole is then heated on a hot plate until the dissolved carbon dioxide has been driven off, when the cover glass is washed off into the dish and removed, and the solution evaporated to dryness, on a hot plate,

covered with a watch-glass and baked on a triangle, at a temperature of at least 200°C . for an hour.

If the material is siliceous or argillaceous and contains a considerable amount of insoluble matter, the method is modified by taking 1 grm. of the finely-ground sample and igniting it in a platinum crucible at the full temperature of the muffle (say, 1050°C .) for about an hour. In this way the whole of the constituents are rendered soluble in dilute hydrochloric acid, unless the material is so siliceous that the lime present is insufficient to flux the whole of the siliceous matter, in which case the material can scarcely be classed as a limestone. The ignited material is cooled in a desiccator and weighed (to determine loss on ignition), transferred to a dish, powdered up with a glass rod, shaken with a little water, and dissolved in hydrochloric acid. The solution, which should be clear, except, perhaps, for a few flakes of precipitated silica, is evaporated to dryness and baked as described above. The object of the baking is to dehydrate the silica, which can be rendered completely insoluble when it is spread out in a thin, even film and treated in this manner.

After baking, the dish is removed from the hot plate, cooled, about 30 c.c. hydrochloric acid (sp. gr. 1.15) added, and the whole digested until solution of all but the silica is effected. The solution is diluted and the silica is filtered off. This is washed, dried, ignited in a platinum crucible in the muffle and weighed. It is then digested with hydrofluoric and sulphuric acids, evaporated, and the residue ignited in the muffle and weighed. The weight of the residue is deducted from the silica, and, if only a few tenths of a milligram, it is added to the ammonia precipitate; if it weighs more than this, it should be fused with potassium bisulphate and analysed. The filtrate from the main silica is returned to the dish, bromine water added sufficient to colour it, and an excess of ammonia added. The solution in the dish is heated just below boiling point, until nearly all the excess of ammonia has been driven off. This stage is one of some delicacy, as the removal of the excess of ammonia is necessary to ensure the precipitation of the whole of the alumina; also the evaporation must not be pushed too far, lest some alumina re-dissolves. The nose is an excellent guide, and the whole of the alumina, the oxides of iron and manganese are precipitated, and the precipitate is free from lime if there is sufficient ammonium chloride present, and the digestion with ammonia has not been unduly prolonged—15 to 30 minutes is sufficient. If the material

is dolomitic it is advisable to re-precipitate both the ammonia precipitate and the calcium oxalate precipitate, so as to ensure freedom from magnesia.

The filtrate from the alumina and ferric oxide is collected in a beaker, and to it about 25 c.c. of ammonia (containing half its volume of ammonia solution of 0.880 sp. gr.) is added. The mixture is brought to its boiling-point and 25 to 50 c.c. of a 4 % solution of ammonium oxalate is poured in (according to whether 0.5 grm. or 1 grm. of material was originally taken). The precipitated calcium oxalate boiled for two or three minutes, allowed to settle for about an hour, and then filtered. The operation, if properly conducted, will separate all but a very trifling proportion of the lime, and the precipitate will be free from magnesia. The possible remnant of lime is recovered at the next operation.

The filtrate from the calcium oxalate is evaporated in a porcelain dish until a pasty residue is obtained, 40-50 c.c. of nitric acid (sp. gr. 1.4) is added, the dish covered, and the heating continued until the ammonium salts have been broken up and their products volatilised.

The residue, after the destruction of ammonium salts, is dissolved in a few c.c. of water and about six drops of hydrochloric acid of sp. gr. 1.15. Excess of ammonia and two drops of ammonium oxalate solution (4 %) are added, and the mixture is heated. A small precipitate is obtained, which is filtered off. In ordinary routine work it usually weighs about 0.0015 grm., and consists of about 0.0010 grm. of silica, and the balance of alumina, ferric oxide, and lime. The two latter belong to the material being analysed, and in specially close work must be separated and added to the values for the main precipitates. Under ordinary conditions this is scarcely necessary. The silica is most probably derived from the glass and porcelain vessels which have been used, and partly, perhaps, from the dust inevitable in a city atmosphere. It is better neglected. The filtrate from this small precipitate contains the whole of the magnesia in concentrated solution, free from excess of ammonium salts, and easy to precipitate cleanly and completely. To obtain it, 10 c.c. of ammonia (50 % of 0.880 solution) and 2 c.c. of a 10 % solution of sodium phosphate are added. On shaking and standing for two hours a well-crystallised precipitate is obtained, which is filtered and washed with ammonia (25 % of 0.880 solution).

The alumina and ferric oxide, and the lime as calcium oxalate, are dried and placed, together with their filter-papers, in platinum crucibles and burnt off gently at the mouth of a gas muffle: when the paper is consumed and the calcium oxalate is decomposed to carbonate or thereabouts, the crucibles are placed inside the muffle and ignited at the full temperature attainable (about $1,050^{\circ}\text{C.}$) for one hour.

The magnesium ammonium phosphate is burnt off, moist in its filter-paper, in porcelain at the mouth of the muffle, brushed out, and weighed as pyrophosphate.

The combined precipitate of alumina and iron oxide is, as a rule, very small, and when only 0.1%–0.3% there is no need to separate them. If larger than this, they should be separated by fusing with potassium bisulphate, precipitating the iron and manganese with caustic soda, the alumina being estimated by difference. If it is necessary to separate the iron and manganese it can be done by the basic acetate method.

For Sulphuric Anhydride.—A second portion of 0.5 gm. of finely-ground material is decomposed as before, and evaporated to dryness in the same way. The contents of the dish are digested with 10–15 c.c. of hydrochloric acid (sp. gr. 1.15), diluted, filtered and washed. The filtrate is boiled, 5 c.c. of a saturated solution of barium chloride added, and the whole boiled for three minutes. After standing for two or three hours, to enable the barium sulphate to assume its most insoluble form, the precipitate is filtered off through a double filter-paper (extra washing is required because of the double paper), and the barium sulphate, moist or dry, together with the filter paper, is ignited at the mouth of a muffle and weighed.

Occasionally limestones, *e. g.* those of the blue lias variety, are met with containing appreciable quantities of pyrites. This constituent is best determined by boiling 1–5 grms. of the finely-powdered sample with aqua regia, removing nitric acid by evaporation with excess of hydrochloric acid, and precipitating the total sulphuric anhydride in the diluted filtered solution by means of barium chloride. In calculating the amount of pyrites present, allowance must be made, of course, for sulphur already existing as sulphuric anhydride in the limestone.

For Loss on Ignition (Carbonic Anhydride and Water).—Unless this has already been done as described above for siliceous material, 0.5 gm. of the finely-ground material is ignited in the muffle at the full temperature of the muffle for one hour.

For convenience this can be done when the main precipitates are ignited.

Carbonic Anhydride.—Various methods are in use for determining carbon dioxide, some of which are described under "control of the mix." The following is a method which has proved to be both accurate and simple, and when the apparatus, Fig. 80, has once been fitted up, yields results approaching the theoretical, whilst requiring very little manipulation.

The potash bulb and guard (sulphuric acid) tube are weighed together and connected up with the apparatus; 0.5 gm. of the sample is placed in the flask and shaken round with a little water. The flask is replaced, and a gentle current of air is drawn through the apparatus. About 20 c.c. of dilute hydrochloric acid is allowed to flow into the flask, drop by drop, through the tap funnel, care being taken to see that the carbon dioxide liberated does not drive the solution back into the soda lime tube. When all the acid is in the flask, the tap is closed and the contents of the flask boiled until the water in the miniature condenser above the flask is too hot to touch, by which time all the more resistant carbonates will have been decomposed. In order to ensure that no carbonic anhydride is left behind, air is drawn through the apparatus for about fifteen minutes, thus displacing any carbonic anhydride dissolved in the silver sulphate solution, etc., and sweeping it on into the solution of caustic potash. The potash bulb and guard tube are then weighed again, the difference between this and the original weight being due to carbon dioxide.

For accurate work it is advisable to wipe carefully the bulb and guard tube, and allow it to stand for 10–15 minutes to gather the "air film" before weighing.

Clay, Shales, Marls, etc.—For cement work the "rational" analysis (estimation of the mineral constituents), of clays, etc., is unnecessary. The method for "ultimate" analysis is as follows:—The dried sample is very finely ground in an agate mortar; 0.5 gm. is fused in a platinum crucible with five to eight times its weight of pure sodium carbonate, until the material is completely decomposed. When cool, the melt is loosened by slightly squeezing the sides of the crucible, transferred to a large dish, preferably of platinum, and digested with about 30 c.c. of hot water until the soluble silicates are dissolved; if the fusion has been properly carried out, the addition of a few c.c. of hydrochloric acid will dissolve the residue, forming a clear

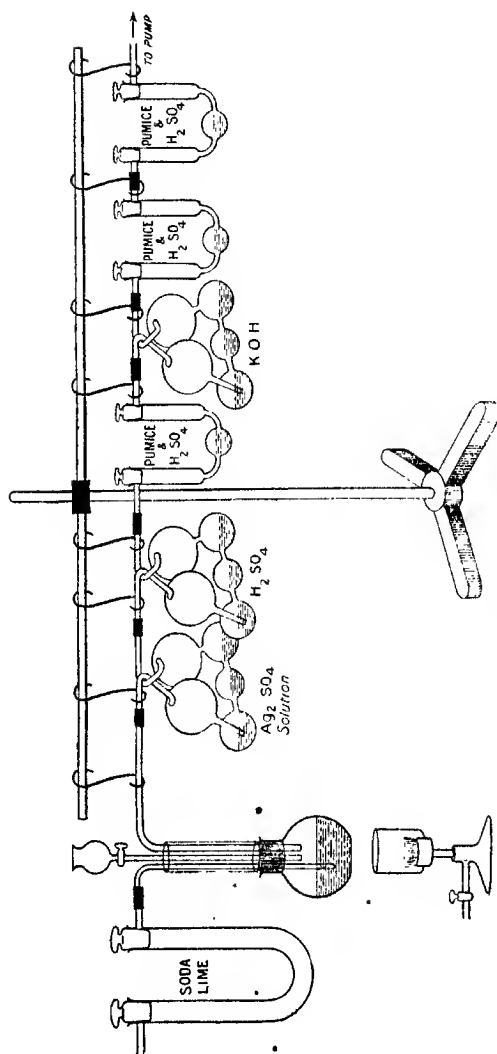


Fig. 89.—Apparatus for determination of Carbon Dioxide.

solution, with possibly a few flakes of silica. (If the acid is added before the fused mass has been properly disintegrated there is a danger of the precipitated silica enclosing alkali, etc.) At this stage it is important to see that there is no loss through "spurting." The solution is evaporated to dryness, and the residue baked on a hot plate for an hour. After cooling, the residue is digested with 30-40 c.c. of hydrochloric acid (sp. gr. 1.15), and diluted with hot water. The insoluble silica is filtered off, washed free from alkali, etc., and dried. For accurate work the filtrate is evaporated and baked again to obtain the small quantity of silica which always remains in solution when the residue, containing a large quantity of sodium chloride, has had but one baking. Apparently the reason for this solubility is due to the insufficient baking of those portions of the siliceous matter which get perched up on to the top of crystals of sodium chloride, etc.

A small quantity of bromine is added to the filtrate, followed by an excess of ammonia, and the whole is digested on the hot plate, just short of boiling, for 15 to 30 minutes, until very little free ammonia is left in solution. The precipitate, which contains practically the whole of the iron, aluminium and manganese, is filtered off, washed and dried. About 10 c.c. of ammonia is added to the filtrate, which is then boiled, and, whilst boiling, an excess of a hot solution of ammonium oxalate is added, and the boiling continued for 3 to 5 minutes, after which it is allowed to stand. (There may not be much calcium oxalate precipitated for some hours. It is necessary to add an excess of ammonium oxalate, as in this solution an appreciable quantity of calcium salts may be present, and yet give practically no precipitate when only one drop of ammonium oxalate is added.)

The calcium oxalate is filtered off, washed and dried. The filtrate is evaporated in a porcelain dish till it becomes pasty, when the dish is covered with a cover glass and 20-30 c.c. of strong nitric acid (sp. gr. 1.4) is added. On warming, the ammonium salts will be broken up, and finally a residue of sodium chloride, with all the magnesia, will be left. When cool, any deposit on the cover glass should be washed into the dish, and the residue dissolved in as little water as possible, to which has been added 5 or 6 drops of hydrochloric acid; a slight excess of ammonia and a few drops of ammonium oxalate are added, and the whole boiled up for a minute or so. The "mess" (a term used for convenience), consisting of traces of silica,

alumina, etc., is filtered off, and 10 c.c. of ammonia and 2 c.c. of a 10 % solution of sodium phosphate are added to the filtrate. After vigorous shaking and allowing to stand for a couple of hours, the precipitate of ammonium magnesium phosphate is filtered off, washed with dilute ammonia (25 % of 0.880 solution), dried, ignited over a bunsen to magnesium pyrophosphate $Mg_2P_2O_7$, cooled and weighed. This weight multiplied by $\frac{40}{111}$ gives the weight of

MgO present. The "mess" is gently ignited and weighed, and if it is more than 1 mgm. or so, it should be analysed by dissolving and separating the silica, alumina and lime; the former is rejected as probably coming from the dishes, whilst the two latter are added to their respective main precipitates.

The three main precipitates are ignited in platinum crucibles at the highest temperature of the muffle for an hour. This is necessary to ensure the thorough dehydration of the silica, alumina, and the complete decomposition of the whole of the calcium oxalate to the oxide instead of leaving a small quantity in the intermediate stage. The complete dehydration of large quantities of alumina and silica is by no means easy, and ignition for an hour at the highest temperature of the muffle is the simplest way to ensure accurate results. In the combined precipitate of iron oxide and alumina there seems to be no risk of any of the ferric oxide being converted to the magnetic oxide by the high temperature, so long as the proportion of alumina to ferric oxide is about normal in a clay. If, however, there is a large excess of ferric oxide, the alumina should be separated and ignited at full temperature separately, and the ferric oxide ignited at low temperature.

After these main precipitates have been cooled and weighed they are treated as follows:—

The silica is treated with a few c.c. of pure hydrofluoric acid, and a drop or two of sulphuric acid, in the weighed platinum crucible and then evaporated to dryness, and the residue ignited, cooled and weighed. The weight of this residue is deducted from that of the crude silica, to obtain the weight of pure silica. The residue, which should be small, consists chiefly of alumina and sodium salts held by the silica, and for accurate work it is necessary to determine the amount of alumina present by fusing with a small quantity of potassium bisulphate, dissolving in dilute hydrochloric acid and precipitating with ammonia. This small quantity of alumina is added to the main precipitate.

The precipitate containing the iron, aluminium, and manganese is fused with about ten times its weight of potassium bisulphate until it is all converted into sulphates.

For this purpose it is necessary to have the precipitate in a fine state of division, and should it be at all sintered into hard lumps, it should be ground in an agate mortar, great care being taken that none is lost, either by "flying" or by being left in the mortar. An alternative method, which in some cases is better, is to use the ammonia precipitate from the "alkalies" portion, instead of this ignited precipitate, for separation of iron, aluminium, and manganese. This obviates the difficulty with the fusion, as solution is effected by direct treatment with hydrochloric acid, and the solution is free from alkalies.

The fused mass obtained by the first method is dissolved in hydrochloric acid; the solution is evaporated to low bulk and poured into an excess of a strong solution of caustic soda. After heating for a few minutes, the solution is poured into a large quantity of cold water, stirred thoroughly, and the precipitate containing the iron and manganese filtered off. The filtrate, containing all the alumina, is generally rejected, the alumina being estimated by difference. If, however, the alumina is required direct, the solution is acidulated with hydrochloric acid, digested with a small excess of ammonia, and the precipitate filtered off and washed. As it is difficult to wash either of these precipitates free from soda, it is necessary to dissolve them in hydrochloric acid and re-precipitate them, the alumina by simple digestion with a small excess of ammonia, and the iron and manganese by the addition of bromine and an excess of ammonia, and boiling for a few minutes. The precipitate of iron and manganese is washed, dried, ignited over a bunsen burner, and weighed. The precipitate is dissolved in a small quantity of hydrochloric acid, by boiling, and the solution evaporated till most of the free acid has been driven off. The solution is just neutralised with ammonium carbonate, and the faintly turbid solution cleared up with a drop of dilute hydrochloric acid; it is then diluted and a few c.c. of neutral ammonium acetate solution added, and the whole boiled for about three minutes, and allowed to stand for a few minutes for the precipitate to settle. If this operation is carried out properly the precipitate of basic ferric acetate will settle quickly, and will be practically free from manganese, and leave only the slightest trace of iron in solution. If, however, the solution remains muddy, or should

there be a large quantity of manganese present, the precipitate should be dissolved and the process of precipitation repeated. If small, this precipitate can be ignited direct to ferric oxide over a bunsen burner, but if large, it is better to dissolve in hydrochloric acid, and re-precipitate with an excess of ammonia before ignition. To the filtrate, containing the manganese, a small quantity of bromine is added, and then an excess of ammonia. As soon as the first reaction is over, the solution is boiled and the precipitate allowed to settle, and filtered off. The precipitate is dried, ignited over a bunsen burner, and weighed as Mn_2O_4 . The manganese in clays, etc., is, however, usually present as manganous oxide (MnO), and consequently the weight obtained should be multiplied by 0.93 to give the quantity of manganese present in terms of MnO .

The lime precipitate is usually so free from foreign matter as to need no further examination, but if it should be necessary, the precipitate is dissolved in dilute hydrochloric acid, which should be rapid and complete if the lime is pure, but if alumina is present it will be difficult to get into solution. A small excess of ammonia is added and the solution boiled, when any iron and alumina present will be precipitated and should be filtered off and re-precipitated to ensure freedom from lime. The filtrate is then boiled with a solution of ammonium oxalate to precipitate the calcium as oxalate; the filtrate is examined for magnesia, with sodium phosphate as described above.

Alkalies.—All clays, shales and marls contain alkalies, and while for cement making it is not always essential to estimate the quantity present, it is often desirable to do so. For this purpose 0.5 to 2 grms. of the finely-ground sample is weighed out, transferred to a fair-sized platinum crucible, and digested for two or three hours with 10 c.c. purest hydrofluoric acid (that supplied in cerasin bottles) and 2 c.c. sulphuric acid (puriss). If necessary, a further 10 c.c. of hydrofluoric acid is added, and the whole gently evaporated till most of the sulphuric acid has been fumed off, great care being taken to prevent loss by "spurting." The anhydrous sulphates are taken up by digesting with hydrochloric acid, and the diluted solution filtered off through a small filter, retaining the insoluble matter in the dish. This is further digested with hydrochloric acid and filtered off as before; if any residuc still remains, which is usually due to insufficient attack, it is washed on to the filter-paper, thoroughly washed, dried, very gently ignited in a platinum crucible, and

the above process of treatment with hydrofluoric acid, etc., repeated.

The original grinding in the agate mortar should be so thorough that further grinding at this stage should be unnecessary, as it might involve loss. In the case of materials such as limestone, etc., the bulk of which can be readily dissolved, the method is modified, in that the material is first digested with hydrochloric acid; the insoluble portion is then treated as above and added to the main solution.

The iron, alumina, and manganese are removed by the addition of bromine and ammonia, and a short digestion. The precipitate is filtered off and thoroughly washed. Ammonia is added to the filtrate and the whole boiled. Ammonium oxalate is added and the whole boiled up again. After the precipitate has been allowed to settle, the calcium oxalate is filtered off, washed thoroughly, and the filtrate gently evaporated to a low bulk. The residuum is then covered, sufficient nitric acid added to destroy the ammonium salts, and, whilst still covered, the whole is evaporated till just dry, or till fumes of sulphuric acid appear. After cooling, the residue is taken up in 2 or 3 c.c. of hydrochloric acid and a little water, and gently evaporated to a low bulk. The solution is diluted, a small excess of a clear solution of barium hydrate added, and the whole digested for about half an hour, during which time a slight skin of barium carbonate should form on top, showing that an excess is present. The precipitate is filtered off and thoroughly washed; the filtrate is digested with excess of ammonium carbonate, and the precipitated barium carbonate filtered off and washed. The filtrate is evaporated to small bulk on a water-bath, a few c.c. of hydrochloric acid are cautiously added, the whole transferred to a small platinum dish, and evaporated to dryness on a water-bath. The residue is very gently ignited over an argand burner to drive off all the ammonium chloride, the crude alkali chlorides are dissolved in a small quantity of water, a drop or two of ammonium carbonate added, and digested for a minute or two, and the whole filtered off through a very small filter with thorough washing into a weighed platinum dish. The filtrate is evaporated on a water-bath, and the residue carefully ignited over an argand, cooled in a desiccator, and weighed. This is the weight of the pure alkali chlorides.

As potash adheres very persistently to all the precipitates and filter-papers, it is absolutely essential that the washings should

be very thorough at all the various stages. It is better to have to remove traces of any slightly soluble precipitate such as magnesia from the crude alkali chlorides than to run the risk of leaving some of the potash in the precipitates or filter-papers.

There are many methods for separating the mixed alkali chlorides, but only two need be described here: the first being the old platinic chloride method, which still seems to be the best where accuracy is required, and the second the perchlorate method, which, if carefully carried out, is good enough for many ordinary purposes.

(1) *The Platinic Chloride Method.*—The alkali chlorides are dissolved in a small quantity of water (and should, of course, leave no residue), and sufficient platinic chloride added to combine with the whole of the potassium and sodium salts and leave a slight excess. The solution is evaporated on the water-bath till it begins to get pasty, then cooled, diluted with a sufficient quantity of 80 % alcohol (by volume) to take up the whole of the sodium salt, and allowed to stand for a few hours. If the quantity of alkali is large, it is better to take up the pasty chlorides in a small measured quantity of hot water, cool, and add sufficient absolute alcohol to bring the final solution to 80 % by volume.

The precipitate of potassium platinic chloride is filtered off, washed with 80 % alcohol till quite free from sodium salts, warmed to drive off the alcohol, and then dissolved by means of boiling water into a weighed platinum dish, evaporated to dryness, dried in an air oven, cooled and weighed. The weight of potassium platinic chloride obtained is multiplied by 0.19343 to give the weight of potash (K_2O) present. The weight of potassium platinic chloride is also multiplied by 0.3068 to give the weight of potassium as chloride, and the difference between this and the weight of combined alkali chlorides gives the weight of sodium chloride. This should be multiplied by 0.53027 to give the weight of soda (Na_2O) present.

(2) *The Perchlorate Method.*—The mixed chlorides are dissolved in from 10–15 c.c. of hot water, and then perchloric acid is added to the extent of two or three times that which is theoretically necessary to precipitate the mixed perchlorates. The mixture is evaporated on a water-bath until fumes of perchloric acid begin to appear, when it is cooled, taken up in water, a c.c. or two of perchloric acid added, and the whole evaporated to fuming again, to ensure removal of hydrochloric acid. It is cooled, and about 20 c.c. of 96 % alcohol containing a small quantity of

perchloric acid (about 0.2 %) added. The mixture is stirred well, to allow the potassium perchlorate, which should be granular, to settle, and filtered through a weighed Gooch's crucible. The precipitate is washed by decantation two or three times, and then washed on to the filter with as little of the alcohol as possible, dried for about half an hour at 120° and weighed. The difference between this and the original weight gives the amount of potassium perchlorate present, and this multiplied by 0.33983 gives the weight of potash (K_2O) present. The weight of potassium perchlorate is also multiplied by 0.5382 to give the weight of potassium chloride which is subtracted from that of the mixed alkalis to obtain the amount of sodium chloride, which, on being multiplied by 0.53027, gives the quantity of soda (Na_2O) present.

Sulphates.—1 grm. of the finely-powdered sample is boiled with about 20 c.c. of hydrochloric acid (50 %), diluted, allowed to stand for an hour or two and the insoluble matter filtered off and washed. The filtrate is boiled and 5 c.c. of a saturated solution of barium chloride is added, and the whole boiled again for three to five minutes. The solution is allowed to stand for two or three hours, the precipitate filtered off through a double filter-paper, and washed with cold water. The precipitate of barium sulphate is dried, ignited and weighed.

Pyrites.—1 grm. of the finely-powdered sample is digested with 20–30 c.c. aqua regia (1 part of nitric acid to 3 parts of hydrochloric acid), evaporated to small bulk and evaporated again to small bulk with hydrochloric acid to remove the remaining portion of nitric acid. The concentrated solution is diluted with about 100 c.c. of water (or more if there is much calcium sulphate present), and when all the soluble matter has dissolved, the residue is filtered off. The filtrate is boiled, 5 to 10 c.c. of a saturated solution of barium chloride added, the whole boiled for 3 to 5 minutes and allowed to stand for 2 to 3 hours. The precipitate of barium sulphate is filtered off through a double filter, washed with cold water, dried, ignited and weighed. As this precipitate will contain the whole of the sulphur present in the sample, whether as sulphate or as sulphide, it is necessary to subtract the weight of barium sulphate obtained by the previous method from the weight of this precipitate in order to obtain that due to sulphide.

Carbon Dioxide.—If the material is calcareous, it may be necessary to estimate the carbon dioxide, and this may be done

in several ways. One of the simplest and most accurate methods is that described in detail under the heading of "Limestone." From 1 to 5 grms. of the material is weighed out into a flask, which is then fitted to a purifying and drying-train. Hydrochloric acid is added, and the whole boiled. The carbon dioxide liberated is swept by means of a current of purified air through a solution of silver sulphate to remove hydrochloric acid gas, then through a sulphuric acid drying-tube, and thence into a weighed potash bulb, where the carbon dioxide is absorbed and can be weighed. By allowing the current of purified air to run for 10 to 15 minutes after the solution has been boiled, any carbon dioxide which had dissolved in the solution of silver sulphate, etc., will be displaced by air and will be carried on into the potash bulb.

Combined Water and Moisture.—In materials like clay, which is a hydrated silicate, it is sometimes necessary to differentiate between combined water and moisture. The latter is easily estimated by taking a weighed quantity of the material, which should be well broken up, dried in an air oven at 110°C .– 120°C ., cooled in a desiccator, and weighed.

In most cases the combined water can be estimated by igniting a weighed portion of the sample at a dull red heat, cooling and weighing. In simple cases the difference in weight, after deducting that due to moisture, will be the amount of combined water present. In most cases, however, the matter is not so simple. Iron is often present in the ferrous state, and this will be oxidised to the ferric state and will make the combined water appear lower than it really is. Similarly, any carbon dioxide which may be driven off will cause an error, by making the combined water appear too high. Pyrites may upset the result either way, according to whether it is completely roasted to oxide, or only to such a stage as will cause sulphate to be left behind.

If it is necessary to estimate the combined water under these conditions, the simplest method is to carry out the ignition in a tube, and collect the water in a weighed U tube, containing pumice and sulphuric acid. Of course, precautions must be taken to prevent errors due to the products of the oxidation of pyrites coming over, and being weighed as water—*e. g.* mixing the material with two or three times its weight of gently ignited lead chromate before ignition.

Titanium.—Most raw materials contain only a trace or so of titanium, and this can be neglected, as it will distribute itself

between the precipitates of silica and alumina, etc. If, however, it should be large, it should be estimated. An absolute guide can always be found in the residue from the hydrofluoric acid treatment of the silica described above. If the residue is at all large, it should be examined for titanium, and if present, the total titanium should be estimated. From 1 to 2 grms. of the finely-ground sample is digested in a platinum crucible with hydrofluoric acid and a drop or two of sulphuric acid, and then gently evaporated until the free sulphuric acid has been fumed off. Cool and fuse the residue with about five times its weight of sodium carbonate. If there is much calcareous matter present, it is better to remove it at this stage by digesting the residue from the acids with a little hydrochloric acid, diluting and precipitating with ammonia as usual. This precipitate, which contains the alumina, titanium, etc., is dried, ignited and fused with sodium carbonate. The fused mass is allowed to cool, transferred to a beaker, dissolved in 150 to 200 c.c. of hot water and boiled for a few minutes. By this means the alumina is dissolved, while the sodium titanate and the iron oxide remain insoluble. This is filtered off, and the residue washed, dried, ignited and fused with ten to fifteen times its weight of potassium bisulphate until it is quite clear. After cooling it is transferred to a beaker, and dissolved in the cold, in 150 to 200 c.c. of water saturated with sulphur dioxide. A little sulphuric acid or hydrochloric acid may be added at this stage to clear the solution. Ammonia is then added to bring it to the neutral point, and a drop or two of hydrochloric acid to keep the solution clear. About 10 to 20 grms. of sodium acetate dissolved in a little water is added, and this is followed by about 30 to 40 c.c. of acetic acid, and the whole boiled for a few minutes. Under these conditions the whole of the titanic oxide comes down in a flocculent condition, which can be easily filtered. The iron remains in solution, unless it is allowed to oxidise by unduly prolonged boiling or filtering. For this reason the solution containing the precipitated titanic acid should be allowed to stand only just long enough to let the precipitate settle, and then rapidly filtered off through a fairly large filter-paper, and washed with hot water acidulated with acetic acid, and as the original solution was saturated with salts the washing must be thorough. The precipitate is ignited and weighed as titanic oxide. If the precipitate is coloured through the presence of iron, or is sintered because the sodium

salts have not been completely removed, it should be fused in potassium bisulphate again and the process repeated.

In the main analysis some of the titanium appears with the silica, and the rest with the ammonia precipitate. The correction for titanium is therefore made by adding the weight of the residue from the silica to the total ammonia precipitate and subtracting the titanous acid from this. If the alumina and iron oxide are separated by means of soda, practically all the titanium will be with the iron, whilst if the iron is estimated by permanganate, the titanium will scarcely affect the titration under ordinary conditions.

Sand.—The sample is finely ground and analysed as described under clay. Owing to the fact that it consists almost entirely of silica, its fusion with sodium carbonate takes place readily. Just one note of warning may be advisable. The small iron and alumina precipitate will probably contain a large proportion of iron, and should not be ignited at too high a temperature lest the ferric oxide (Fe_2O_3) be reduced to the magnetic oxide (Fe_3O_4).

If it is not necessary actually to estimate the silica, a much quicker method is to digest the finely-ground sand with hydrofluoric acid and a drop or two of sulphuric acid, in order to remove the silica. After evaporation to fuming, to remove the hydrofluoric acid, the small residue of anhydrous sulphates may be taken up in hydrochloric acid and analysed.

PORTLAND CEMENT

(1) *For Silica and Chief Bases.*—0.5 grm. is placed in a shallow dish about 6 in. in diameter, swirled round with a few c.c. of water until thoroughly mixed. About 20 c.c. of hydrochloric acid of sp. gr. 1.15 are added, and the swirling continued for a few minutes. The cement is thus dissolved almost completely, and no silica is precipitated. The dish with its contents is placed on a hot plate, taken to dryness, covered with a clock-glass, and baked on a triangle at a temperature of at least 200°C . for an hour. This part of the procedure is essential. Silica can be rendered insoluble when it is spread out in a thin, even film and heated in this manner.

The residue obtained on evaporation in the manner described is digested with about 30 c.c. of hydrochloric acid of sp. gr. 1.15, and the silica, together with the insoluble residue, is filtered off. The filtrate is returned to the dish in which the cement was

dissolved, and an excess of ammonia added. The solution in the dish is gently heated until nearly all the excess of ammonia has been driven off. This stage is one of some delicacy. The removal of the excess of ammonia is necessary to ensure the precipitation of the whole of the alumina: also the evaporation must not be pushed too far, else some alumina may redissolve. No guide is so reliable as a well-trained nose. When properly conducted the separation is exact, the whole of the alumina and ferric oxide is precipitated, and the precipitate is free from lime.

The filtrate from the alumina and ferric oxide is collected into a beaker, and to it about 25 c.c. of ammonia (containing half its volume of solution of 0.880 sp. gr.) is added. The mixture is brought to its boiling-point, and 25 c.c. of a 4 % solution of ammonium oxalate is poured in. The precipitated calcium oxalate is boiled for two or three minutes, allowed to settle for about an hour, and then filtered. The operation, if properly conducted, will separate all but a very trifling proportion of the lime, and the precipitate will be free from magnesia. The possible remnant of lime is recovered at the next operation.

The filtrate from the calcium oxalate is evaporated in a porcelain dish until a pasty residue is obtained, 40-50 c.c. of nitric acid (sp. gr. 1.4) is added, the dish covered, and the heating continued until the ammonium salts have been broken up and their products volatilised.

The residue, after the destruction of ammonium salts, is dissolved in a few c.c. of water and about six drops of hydrochloric acid of sp. gr. 1.15. Excess of ammonia and two drops of ammonium oxalate solution (4 %) are added, and the mixture is heated. A small precipitate is obtained, which is filtered off. In ordinary routine work it usually weighs about 0.0015 grm., about two-thirds of which is silica, and the balance of alumina, ferric oxide, and lime. The two latter belong to the cement, and in specially close work must be separated and added to the values for the main precipitates. Under ordinary conditions this is scarcely necessary. The silica is most probably derived from the glass and porcelain vessels which have been used, and partly, perhaps, from the dust inevitable in a city atmosphere. It is better neglected. The filtrate from this small precipitate contains the whole of the magnesia in concentrated solution, free from excess of ammonium salts and easy to precipitate cleanly and completely. To obtain it, 10 c.c. of ammonia

(50 % of 0.880 solution) and 2 c.c. of a 10 % solution of sodium phosphate are added. On shaking and standing for two hours a well-crystallised precipitate is obtained, which is filtered and washed with ammonia (25 % of 0.880 solution). The various precipitates are dealt with as follows—

The silica and insoluble residue, the alumina and ferric oxide, and the lime as calcium oxalate, are dried and placed, together with their filter-papers, in platinum crucibles and burnt off gently at the mouth of a gas muffle; when the paper is consumed and the calcium oxalate decomposed to carbonate or thereabouts, the three crucibles are placed inside the muffle and ignited at the full temperature attainable (about 1,050° C.) for one hour. Two sets of precipitates are commonly worked off in a single muffle.

By this means all are brought to the state of anhydrous oxides, and, except in rare cases, need no re-ignition. The magnesium ammonium phosphate is burnt off moist in its filter-paper in porcelain at the mouth of the muffle, brushed out, and weighed as pyrophosphate.

(2) *For Insoluble Residue and Sulphuric Anhydride.*—A second portion of 0.5 grm. of cement is decomposed as before, and evaporated to dryness in the same way. As it is not intended for the determination of silica, there is no need to bake the residue. The contents of the dish are taken up in 10–15 c.c. of hydrochloric acid of sp. gr. 1.15 and filtered, leaving as much as possible of the residue in the dish. The silica on the filter is washed back into the dish and digested with a saturated solution of sodium carbonate. The whole of the silica active and useful in the cement is dissolved, and the inert silicates are left.

This insoluble residue is thoroughly washed, ignited at the mouth of a gas muffle and weighed, and the weight is deducted from that of the silica plus insoluble residue obtained from the previous portion, thus giving the quantity of combined effective silica.

The original acid solution from the second portion of 0.5 grm. is precipitated with 5 c.c. of a saturated solution of barium chloride at the boiling temperature. The boiling is continued for about three minutes, and after standing for one or two hours, the solution is filtered and the barium sulphate, together with the filter-paper, is ignited at the mouth of a gas muffle and weighed.

(3) *For Loss on Ignition; Carbonic Anhydride and Water.*—0.5 grm. of the cement is ignited in platinum for half an hour in

a gas muffle at a temperature of about 800° C. If this temperature is exceeded there may be a loss of sulphuric anhydride.

(4) *For Carbonic Anhydride*.—2 to 5 grms., according to the character of the cement, are decomposed with hydrochloric acid in the ordinary manner, and the carbonic anhydride, after purification through a silver sulphate tube and drying, as usual, is collected in a weighed potash bulb.

(5) *For Alkalies*.—1 gm. of the cement is decomposed with hydrochloric acid in the way already described, and the silica and chief bases got out as usual. The ammonium salts are destroyed with nitric acid, and the final residue, containing magnesia and alkalies, is treated with baryta and afterwards with ammonium carbonate, and the alkalies are converted into chloride, weighed as such, and separated by the use of platinum chloride, as described on p. 171.

(6) *Separation of Alumina and Ferric Oxide*.—This may be carried out on the mixed precipitate after ignition, or on a separate portion of cement. In the former case the precipitate is fused with potassium bisulphate and the melt dissolved in hydrochloric acid. The solution is precipitated with ammonia, dissolved in hydrochloric acid, the solution concentrated, and poured into excess of caustic soda (prepared from the metal). The alkaline solution is heated to near boiling, to ensure the dissolution of the alumina. The operation is best conducted in platinum. The solution is diluted so as to allow it to be filtered through paper, and the ferric oxide collected, dissolved in hydrochloric acid, and precipitated with ammonia, filtered, ignited and weighed. The ignition may be performed over a bunsen burner, as there is not the same difficulty in completely dehydrating ferric oxide as there is with alumina. If desired, and as a check, the alumina is recovered from the caustic soda solution.

It is generally more convenient to obtain the joint ammonia precipitate from another portion of the cement, and to separate the ferric oxide and alumina in this by the caustic soda process; the bisulphate fusion and recovery of the oxides from the melt are thus avoided. In the event of manganese being present in sensible amount, as it is in Roman and Medina cements, and in cements made from blast-furnace slag or adulterated with the same material, the ammonia precipitation must be carried out in the presence of bromine. By using a little bromine throughout, the manganese finally appears with the iron, and can be satisfactorily separated by a basic acetate precipitation.

A more rapid determination of iron, sufficiently accurate for all practical purposes, may be made as follows: 1 gm. of cement is treated with water and dissolved by the addition of a few c.c. of hydrochloric acid in a small conical flask. After solution, 3-4 grms. of pure granulated zinc (free from iron) are added and the flask closed with a cork fitted with a bunsen valve. When all the iron has been reduced to the ferrous state, and the zinc dissolved, the cooled solution is poured into 200-300 c.c. air-free distilled water, excess of sulphuric acid added, and titrated with $\frac{N}{20}$ KMnO_4 solution. Since the reagents used are never

absolutely free from iron, it is advisable to make a blank determination under exactly the same conditions prevailing in the actual estimation, and make a correction for this.

(7) *For Sulphides.*—In general, these are present in such small quantity that they may be ignored. They are, however, of more importance when slag products are treated. The best process is to dissolve the cement in hydrochloric acid in an atmosphere of coal gas, and collect the sulphuretted hydrogen in lead acetate solution, finally weighing the precipitated sulphide as lead sulphate.

These details of analytical methods have been given at some length, as they are the outcome of much practical experience, and if followed carefully will give accurate results. The principles are, of course, known to every chemist, but small practical methods of procedure carefully described may prevent grave errors.

CHAPTER IX

CHEMISTRY OF PORTLAND CEMENT

A LARGE amount of very valuable work has been done by many investigators on the chemistry of cement. The analytical side and mechanical testing of cement have been already dealt with in a foregoing part of this book, and it remains to consider the chemistry proper of cement. This is still unsettled, but what follows is based on the researches of Henri Le Chatelier, whose book on *The Constitution of Hydraulic Mortars* (translated by Joseph Lathrop Mack) remains a classic. Although the original work was done in 1887, it has been repeatedly criticised and revised, so that it may be taken as the basis of our modern knowledge of cements. The mode in which the building up of current theory has taken place may well be illustrated by quotations from Le Chatelier's original memoir.

The fundamental idea concerning the mode of setting of cement is best expressed in Le Chatelier's work on plaster of Paris. It is made clear by the following paragraph.

"The physical phenomenon of the crystallisation of plaster during its setting would then be as follows: calcined plaster is hydrated in contact with the water, which has been used to temper it, and gives a solution which soon allows the hydrated sulphate to crystallise, and then becomes able to dissolve new quantities of dehydrated sulphate. The phenomenon continues in this manner until the complete hydration and crystallisation of the plaster. Indeed, these two contrary actions occur simultaneously at adjacent points. A continuous solution of new quantities of plaster compensates for the impoverishment of the liquor resulting from the equally continuous deposition of the hydrated crystals. The degree of concentration at which the solution is maintained depends upon the relative speed of these two contrary phenomena. When the hydration is very slow, the supersaturation is weak. When it is rapid, on the contrary, the supersaturation

If this explanation is the true one, it must follow that the points where the hydrated crystals deposit are not necessarily in the places occupied by the grains of plaster. This is what has been confirmed by following the hydration under the microscope. Large needles are seen to form in the middle of the voids filled with water.

It is comparatively easy to prepare definite anhydrous and hydrated silicates of barium, and the work done on these has been a useful stepping-stone to that on calcium silicates, which mostly concern us. The preliminary work in Le Chatelier's experiments relates to such matters as the dissociation of calcium carbonate, and although of great value as leading up to the preparation of Portland cement, would be out of place here, where the brochure mentioned above is readily accessible. But when we come to the description of the reactions actually occurring in the manufacture of Portland cement, the matter is somewhat different. I may say at once that I have not been able to make up my mind completely on this point, and therefore the only reasonable course is to record the best opinion. Dismissing the work of the earlier experimenters, I come to Le Chatelier's own views, and quote a portion of his statements.

Simple Calcium Silicates—Anhydrous Silicates

" $\text{SiO}_2 \cdot \text{CaO}$.—This silicate has been known for a long time. It exists in nature, where it has been called wollastonite; it has been produced by different means in the laboratory. I have prepared it by fusing a mixture of lime and silica in suitable proportions in a common plumbago crucible. A very hard mass, with crystalline fracture and full of cavities, is obtained. When examined in a thin plate in the polarising microscope, it is discovered that the crystals are present in thin, wide plates, which, viewed through their edge, show a very strong double refraction, and, on the contrary, viewed through their depth, a very weak double refraction, if any.

"This silicate, when finely pulverised and digested in the cold for several days, in pure water, in solutions of ammoniacal salts, or in lime water, does not undergo any kind of alteration, which demonstrates that it cannot take any part in the normal hardening of cements. It is rapidly attacked by the strong acids with the production of gelatinous silica; it is slowly attacked by the weak acids such as carbonic acid. Tempered with water, charged with carbonic acid and left in an atmosphere of carbonic acid, it sets

completely. This fact has also been observed by M. Landrin, and has been the basis for one of his theories upon the set of cements.

" $\text{SiO}_2 \cdot 2\text{CaO}$.—The compound corresponding to this formula ought to belong to the family of peridotites; it does not exist in nature, and has not been obtained until now in the laboratory.

"I have produced it by the direct fusion of silica and lime in suitable proportions. The temperature necessary to obtain the fusion is near the melting-point of wrought-iron. A mass is thus obtained which, withdrawn quite hot from the crucible, is compact, very hard, and can only be broken with difficulty by the hammer.

"On the contrary, on letting the crucible cool before opening it, only a white pulverulent mass is found, identical in appearance with the mixture experimented upon. The combination is none the less complete because the action of acids gives immediately a deposit of gelatinous silica. The fact is that during the cooling a very interesting phenomenon occurred, which can be observed by leaving in the air the mass which was taken out of the crucible while quite hot. The mass, absolutely compact at first, is seen to crack gradually, to swell up, to disintegrate progressively, and finally to be reduced to a white powder like slaked lime in appearance. When examined under the microscope, this powder is formed of prismatic fragments with weak double refraction diminishing in the direction of their greatest length, and sometimes showing fine striae following this direction.

"This phenomenon of spontaneous pulverisation has long been known in the metallurgy of iron: it is observed with all blast-furnace slags which are sufficiently calcareous. Hitherto, this pulverisation has been attributed to the action of the atmospheric moisture, which leads to a slaking of slags by hydration as it does with quick-lime. The same phenomenon is also observed in the manufacture of Portland cement. Frequently, fragments of cement clinker withdrawn while hot from fire are seen to pulverise at the end of a certain time. This transformation would be accompanied by a disengagement of heat, manifested in the dark by a new incandescence of the already cooled material. The value of this powder as cement is very slight, therefore its production is an important cause of loss in manufacture. The study of this question thus has a direct interest at this point.

"I began by assuring myself that this property belonged to the silicate $\text{SiO}_2 \cdot 2\text{CaO}$, and only to it, and consequently the spontaneous pulverisation in cements and slags is a certain indication of

the presence of this compound. By varying the relative proportions of silica and lime submitted to fusion, it is proven that the pulverisation is the more slow and incomplete the more the composition corresponding to the formula above is departed from. The mixture $\text{SiO}_2 \cdot 1\frac{1}{2}\text{CaO}$ gives some unpulverised fragments large enough to enable thin sections to be cut from them. The very brilliant edges, with very strong double refraction, indicate the presence of wollastonite. This shows in passing that the puzzoportland of M. Landrin does not exist as a definite product, and that it is only a mixture of the two silicates $\text{SiO}_2 \cdot \text{CaO}$ and $\text{SiO}_2 \cdot 2\text{CaO}$, both of which keep their individual properties. By replacing part of the lime in the compound $\text{SiO}_2 \cdot 2\text{CaO}$ by magnesia, its pulverisation is again diminished. For equal molecular ratios of lime and magnesia a mass is obtained which remains absolutely compact, hard and clearly crystallised: it is monticellite (CaMgSiO_4). The addition of alumina and iron oxide also diminishes the pulverisation. Thus it is that blast-furnace slags often require many days to disintegrate, and only occasionally give a coarse sand, very different from the impalpable meal produced by the pure calcium peridote."

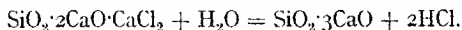
Researches on grappiers, which are the hard core left when some cement-making materials of the hydraulic lime class are burnt and ground, gave Le Chatelier the notion that it is possible to prepare tricalcium silicate, and that that would be established as the essential constituent of Portland cement. His words are: " $\text{SiO}_2 \cdot 3\text{CaO}$.—Tri-basic silicates of protoxides are unknown; however, some analyses of grappiers, or hard-burned lumps from siliceous hydraulic limes, have led me to foresee the existence of a silicate corresponding to the formula given above. But for a long time all my attempts to prove it synthetically have remained fruitless. The calcination of a mixture of silica and lime has given me only a mixture of calcium silicates and free lime. This latter is recognised by the rapid disengagement of heat, and by the slaking produced by the action of water. But after slaking, the pulverulent mass, tempered with water, sets more or less slowly, thus behaving like a true hydraulic lime. This seems to indicate that among the silicates obtained there must be one which is different from the silicates previously studied. But this indication is too slight to base any conclusion upon.

"I have hoped to obtain the best results by approximating the practical conditions of the manufacture of these cements;

that is to say, by using a flux to facilitate the reaction of the silica and lime. Calcium chloride was clearly indicated by its great fusibility and its solubility in water and alcohol, which ought to allow its easy separation from the crystals. By using an excess of calcium chloride, I have obtained very pretty crystals, unchanged by alcohol, but very easily changed by water. These ought, therefore, to be crystals of cement.

"Chemical analysis showed me that, instead, I was dealing with a calcium chlor-silicate—

"I then had the idea of starting from the calcium chlor-silicate previously obtained, and decomposing it by water vapour at a temperature above 450° C., the normal dissociation temperature of calcium hydrate. I obtained in this way the reaction—



"The decomposition is very slow and remains superficial. The mass must be pulverised repeatedly in order to obtain a nearly complete elimination of chloride. The purest product thus prepared had the composition.

	Observed.	Calculated.
SiO ₂ (by difference)	26.7	26.3
CaO (tested alkalinometrically)	72.1	73.7
CaCl ₂ (tested by silver)	1.2	—
	<hr/> 100.0	<hr/> 100.0

"This is a pulverulent mass, showing no evident trace of crystallisation: it is not, therefore, possible to establish by fixed characteristics if we are really dealing with a definite compound, and consequently if it is identical with crystals of cement. But by finely pulverising this mass, tempering it with water and allowing it to harden in boiling water, there is obtained, at the end of eight days, briquettes which are comparable in hardness to those of cement, and showing no trace of swelling or cracking. This absence of swelling is a certain indication of the absence of free lime (because, in fact, if we added only 1 % of strongly calcined free lime to a cement of good quality which does not swell in cold water, we observe a considerable cracking and a swelling of volume of about 10 %). This characteristic, together with the property of setting which none of the lower silicates possess, shows clearly that we have to do with a compound and not a simple mixture whose properties would simply be the sum of those of the mixed bodies."

Various calcium aluminates have been prepared, such as $\text{CaO} \cdot \text{Al}_2\text{O}_3$, $3\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, and their products of hydration are found capable of setting.

Going back to the original view that such hydratable substances set by alternately forming supersaturated solutions, then depositing crystals, and so proceeding on unhydrated materials in the same way—a view accepted as true for plaster of Paris—I find little direct evidence that this progressive hydration holds for any of the essential constituents of Portland cement, particularly of the most important $3\text{CaO} \cdot \text{SiO}_2$.

It may be interesting to trace the progressive movements of thought. Le Chatelier's early work, which is really the foundation of our knowledge, has been referred to.

In 1906, I read a paper before the Society of Chemical Industry, part of which I transcribe—

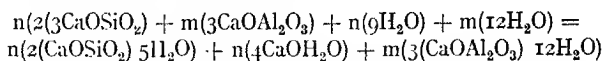
“ The two chief methods which have been successfully employed in investigating the chemistry of cement are the synthetic and the microscopical. All analytical methods have failed, as they have failed when applied to the determination of the proximate composition of natural rocks. By synthesis three calcium silicates, CaOSiO_2 , 2CaOSiO_2 , 3CaOSiO_2 , have been prepared and are recognised as individual bodies; the four aluminates, CaOAl_2O_3 , $3\text{CaO} \cdot 2\text{Al}_2\text{O}_3$, $2\text{CaOAl}_2\text{O}_3$ and $3\text{CaOAl}_2\text{O}_3$, have similarly been prepared and identified. It is generally accepted that of these, tricalcium silicate, 3CaOSiO_2 , is the essential constituent of Portland cement. The constituent of next importance is a basic aluminate, but there is still some difference of opinion as to whether this body should be represented by the formula $3\text{CaOAl}_2\text{O}_3$ or $2\text{CaOAl}_2\text{O}_3$. The remaining silicates and aluminates are of minor moment, and their presence in Portland-cement clinker may be regarded as due to the natural imperfection of the raw materials employed and the limitation of the means of uniting these raw materials under the conditions of manufacture at present obtaining. In short, if a mixture of tricalcium silicate and tri- (or di-) calcium aluminate in suitable proportions could be industrially prepared, it would be an ideal cement. The silicates and aluminates going to make up commercial Portland-cement clinker, whether essential or subsidiary, are not necessarily present in the clinker as separate individuals. There is good reason to believe that they exist as solid solutions, and that these solid solutions may have been mingled whilst the clinker was plastic, and have

separated out when it cooled. The two chief minerals which have been recognised in cement clinker have received the names alite and celite, and, according to the best current knowledge, consist respectively of a solid solution of tricalcium aluminate in tricalcium silicate, and one of dicalcium aluminate in dicalcium silicate. Of these two substances, alite alone is of value in the setting of the cement. It is generally accepted that in normal Portland-cement clinker containing only moderate quantities of ferric oxide, magnesia, and alkalis, these minor constituents play quite a subsidiary part. No doubt they contribute to the fusible magma from which the main minerals crystallise, but the fact that what is truly Portland cement can be prepared from materials in which they are absent is sufficient proof of their relative insignificance. Whether any modification of this very clear and simple view of the constitution of Portland-cement clinker may later be found necessary or not, it is in my judgment the nearest approach to the truth yet obtained, and on account of its philosophic basis, no less than because of its experimental foundation, it is as far in advance of the explanations current twenty years ago concerning the chemistry of cement as the manufacture of to-day is ahead of that at the same earlier date.

"It will be observed that this theory does not necessarily apply to cements, such as Roman cement, less basic than Portland cement, or containing substantial quantities of constituents which are subsidiary in Portland cement, as, for example, natural cements rich in magnesia. Each of these will have to be examined on its merits, but although the inquiry will be far from a repetition of the Portland-cement investigation, yet its successful prosecution will be greatly aided by the knowledge already at our disposal.

"Correspondingly with the establishment of a good working hypothesis of the constitution of Portland-cement clinker, has grown a reasonable explanation of the chief changes which occur when Portland cement sets, and it may fairly be said that this explanation has been reached during the period with which I am dealing. The underlying idea is derived from researches on the setting of plaster of Paris which is known to be due to the dissolution of a more soluble form of calcium sulphate and the deposition of a less soluble form in felted crystals, the dissolution and deposition being successively accomplished by the agency of a quantity of water, small relatively to the mass of solid matter dissolved and deposited. This idea can be applied to those constituents of

Portland cement which are soluble in water and will form hydrated crystalline products, provided that the substances dissolved have a transient greater solubility than the substances deposited. Now, in Portland cement the most important constituent, alite (*i. e.* a solid solution of tricalcium aluminate in tricalcium silicate), is affected by water; and celite, the second large constituent, is but little influenced. Alite, when acted on by water, is decomposed according to the equation—



n and m being written in merely to recall the fact that alite may contain various proportions of its two components, tricalcium silicate and tricalcium aluminate. It is believed that the tricalcium aluminate, once liberated from its solid solution in tricalcium silicate, goes through the stages of hydration, dissolution in a more soluble form, and deposition in a less soluble form, by the action of a relatively small quantity of water as an intermediary,¹ precisely as does hemihydrated calcium sulphate when plaster of Paris sets. The behaviour of the tricalcium silicate is not quite so simple. On liberation from its solid solution it is decomposed, yielding hydrated monocalcium silicate and calcium hydroxide. Both crystallise and form a hard coherent mass. It must be assumed that one or both substances possess two degrees of solubility if the plaster hypothesis is to be used. Unfortunately, there is not, as far as I know, any direct evidence on this question. The dual solubility of hydrated monocalcium silicate has not been established, and that of calcium hydroxide, though it exists, is dependent on alteration of temperature, and is not a transient phenomenon occurring at the time of dissolution. It is possible that these two substances are mutual solvents, and communicate to each other the necessary property of transition from a higher unstable solubility to a lower stable solubility. If no proof of this is forthcoming, the plaster theory may have to be displaced."

This was what I wrote in 1906. Later, the alite, belite and celite theory had been somewhat discounted, and I was asked to deliver a lecture before the Institute of Chemistry, in October 1912, and append a few notes.

¹ I do not know whether any direct experiments on this point have been made.

"As it is impracticable to prepare Portland cement having the proportions indicated by the equation,

$$\frac{\text{CaO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3} = 3.$$

on a manufacturing scale, and to cause the acid and basic oxides there represented to unite perfectly, it is necessary that, to ensure the absence of uncombined lime, the acid oxides should be somewhat in excess and the ratio given be slightly below 3. It follows that in addition to tricalcium silicate and tricalcium aluminate, there will necessarily be present a lower silicate, namely, the orthosilicate $2\text{CaO}\cdot\text{SiO}_2$, and probably a lower aluminate (e.g. $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ and $\text{CaO}\cdot\text{Al}_2\text{O}_3$) and, in addition, such minor constituents as magnesia and oxide of iron, free or combined. We know too little of the rate at which union of the chief basic and acid oxides can be induced to take place at a merely sintering temperature to allow us to do more than approach the limit set above, but it is reasonable to conclude that the closer the approximation the better the product. As an example may be given the percentage composition of a cement composed of tricalcium silicate, tricalcium aluminate and dicalcium silicate in such proportions that an ample supply of alumina is present (5 %) to induce the formation of tricalcium silicate, and that the ratio of acid to basic oxides shall not exceed 1 : 2.9 is—

	Per cent.	Corresponding with	Per cent.
SiO_2	23.49	$3\text{CaO}\cdot\text{SiO}_2$	79.11
Al_2O_3	5.00	$3\text{CaO}\cdot\text{Al}_2\text{O}_3$	13.23
CaO	71.51	$2\text{CaO}\cdot\text{SiO}_2$	7.66
	<u>100.00</u>		<u>100.00</u>

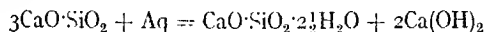
"A cement of this composition would terrify the average user; but, according to the best knowledge we now possess, it would be perfectly safe and of admirable quality.

"In like manner, if a cement be constructed consisting of 20 equivalents of tricalcium silicate, 1 of tricalcium aluminate and 1 of dicalcium silicate, it will have the ultimate composition—

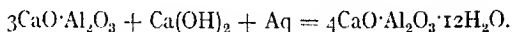
	Per cent.
SiO_2	25.19
Al_2O_3	2.04
CaO	72.77
	<u>100.00</u>

an even more blood-curdling compound, but one which quite possibly could be made, and, if made, could certainly be safely used.

"The chemical changes accompanying the setting of Portland cement have been the subject of almost as much study and dispute as has the constitution of the cement itself. Two views are now current and worthy of attention. The first is that the cementitious calcium silicates and calcium aluminates are hydrated and caused to crystallise in the same way as that generally accepted to be true of plaster of Paris—that is, the water used in gauging dissolves a portion of these bodies and forms a super-saturated solution which then deposits crystals of the hydrated compounds and renders the water competent to dissolve another portion of the anhydrous substances, again to form a super-saturated solution, and again to deposit crystals. Now that tricalcium silicate has been rehabilitated, no better representation can be given than that shown by the original equations of Le Chatelier—



and



"It will be observed that in the act of setting, two-thirds of the whole of the lime pertaining to the tricalcium silicate is set free, and that, even allowing for the combination of a part of this with tricalcium aluminate to form the tetra calcium aluminate (hydrated), there will be a substantial quantity over, as in fact there is.

"It must not be assumed that there has been rigorous proof of all stages of this explanation, but it is consonant with those facts which are known, and is based on the careful and conclusive work which has been done on the setting of plaster of Paris.

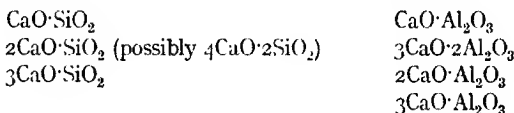
"The second view of the setting of Portland cement is sharply differentiated from the foregoing in that the essentially cementitious product is believed to be a 'gel,' and depends on the observation that when the hydration of finely-powdered cement is watched under the microscope gelatinous products are formed which are regarded as hydrated calcium silicates and aluminates in a colloidal condition. That gels are formed is indicated by their power to absorb dyes and become stained, and it is considered that in process of time they take up lime set free by the gradual hydration of the calcium silicate and become indurated.

"It is not an agreeable position to be in when one finds oneself unable to pronounce a definite opinion on two hypotheses so different; but in this case I am forced to it because the data available on both sides appear to me scanty, sketchy or inconclusive, and my own observations, made for some technical purpose and necessarily worse than sketchy as a research, have led me to nothing worthy of your consideration. I incline to the crystalline theory, but then the notion of a kind of glue sticking things together—a cement within a cement—is very attractive. I could cite no better instance than this as an example of a matter of primary interest to a great industry, and still not decided by us chemists."

A summary of recent views prepared entirely irrespective of the writer's opinion may be appended.

My friend and late assistant, Mr. Gilbert. J. Alderton, B.Sc., F.I.C., was good enough to go through the latest literature, and I gladly acknowledge his help. This precis, bringing the date to 1906, is as follows—

Synthetical Investigation.—In view of the possibility of the formation of numerous solid solutions of varying composition, one must hesitate to accept outright the existence of definite chemical compounds of the nature of silicates and aluminates; but it seems reasonable to believe that the following compounds, at least, have been definitely prepared and examined—



The existence of complicated so-called silico-aluminates seem to be questionable (Richardson has shown them to be solid solutions of indefinite composition). Various investigators—*e.g.* Zulkowski¹ and Meyer²—have assigned structural formulæ to many of the above compounds, but we must hesitate to accept them in the present state of our knowledge. The contention of Zulkowski and Meyer that there are two isomeric forms of the dicalcium silicate, $2\text{CaO} \cdot \text{SiO}_2$, also needs experimental confirmation.

Newberry³ states that Le Chatelier, Rebuffat, Meyer, and Zulkowski were unsuccessful in preparing $3\text{CaO} \cdot \text{SiO}_2$, but only

¹ *J. S. C. I.*, 1901–2.

² Tricalcium Silicate. *Thonin Zeit.*, 1902.

³ The Constitution of Portland Cement. *J. S. C. I.*, 1897.

mixtures or solutions of free lime in a lower silicate. It has, however, been prepared by Newberry, Rohland and Richardson.

This must be contrasted with the definite statement of Le Chatelier, based on very careful and detailed experimental work.

Richardson¹ seems to have proved that various so-called complex silico-aluminates are not definite compounds, but solid solutions of indefinite structure.

Various compounds of iron and magnesia, with lime and alumina, are known to exist, but they are of minor importance.

Constitution of Portland Cement.—Microscopic work of Le Chatelier and Törnebohn has shown the existence of definite mineral constituents—alite, belite, celite, and felite, besides an amorphous mass.

Portland cements are formed essentially of a calcium silicate differing but little from the formula $3\text{CaO}\cdot\text{SiO}_2$, which is the active element of hardening and is produced by the chemical precipitation in the midst of a molten double silicate which has acted as a vehicle for the silica and lime, to allow them to combine but remaining sensibly neutral during their hardening.

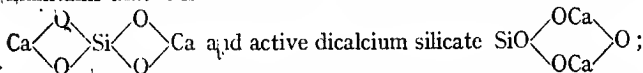
This original view of Le Chatelier's is the most reasonable one to-day and has been confirmed by numerous investigations of Meyer, Rebuffat, Michaelis and Ludwig. Finely-divided SiO_2 and CaO will combine at the temperature of the cement kiln, but the resulting silicate is not crystalline, is porous, and only hardens imperfectly with water. To obtain a dense crystalline silicate a sufficient temperature is necessary to fuse this compound. In the presence of other substances which act as a flux, such as Al_2O_3 and Fe_2O_3 , the silicate separates gradually from the more or less fusible mass in a crystalline form, which during cooling remains enveloped in a non-crystalline magma of indeterminable composition.

The work of Meyer, Ludwig, etc., has failed to clear up the constitution of the magma, and Le Chatelier's view is the most simple and reasonable. Newberry states, that "without doubt the idea of Le Chatelier, Meyer and Ludwig that in commercial Portland cement the magma is a non-crystalline substance containing practically all the iron and alumina, and of a variable composition, is correct."

On the other hand, one or two observers do not agree with Le Chatelier and the rest, that $3\text{CaO}\cdot\text{SiO}_2$ is the composition of the

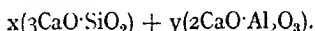
¹ Portland Cement as a solid solution. *J. S. C. I.*, 1903.

essential constituent of Portland cement. Rohland regards it as a solid solution of lime in a less basic silicate. Zulkowski maintains that it is a mixture of inactive dicalcium orthosilicate



the latter is hydraulic. According to Zulkowski, quick cooling forms the active hydraulic (the meta-silicate), whilst slow cooling results in a mixture of the two isomers. This theory rests on somewhat feeble grounds, and lacks confirmation.

According to Le Chatelier, the principal aluminate in Portland-cement clinker is $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, and it is on this point that the Newberrys differ most. The latter maintain that Al_2O_3 exists mainly as $2\text{CaO} \cdot \text{Al}_2\text{O}_3$, and give the following formula for pure Portland-cement clinker.



The part played by Fe_2O_3 in Portland-cement clinker is not clearly understood. It evidently combines with lime like alumina, and its compounds are more fusible than those of alumina: in fact, its function seems to be little more than that of a flux to aid the combination of $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ and CaO . Ludwig states that iron exists in the ferrous state in Portland-cement clinker, and also that Fe_2O_3 never acts as an acid; both statements are against practical experience. The whole question relative to the state of Fe_2O_3 and Al_2O_3 in cement demands new experimental researches.

Fe_2O_3 plays an unimportant part in setting and hydration of Portland cement.

Magnesia probably acts like lime, but is less active. The Newberrys neglect it in their calculations because they decided that it could not give a hydraulic product if present in cement. Zulkowski says that magnesia is undesirable because it hydrates with greater difficulty than CaO , and may give rise to fissures in well-worked cements. He comes to the conclusion that it is only the free magnesia which is the cause of the evil.

Physico-Chemical Theory.—The development of this theory by Richardson, Rohland, etc., is a noteworthy feature of recent years. Richardson mentions that Portland-cement clinker can be satisfactorily explained as a heterogeneous solid solution. There are two main constituents of cement clinker which Richardson identifies with Törnebohn's alite and celite. These are two

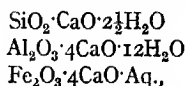
solid solutions, of different degrees of basicity, which have been crystallised from a more or less mobile magma on cooling.

Alite = solid solution of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ in $3\text{CaO} \cdot \text{SiO}_2$.
 Celite = " " " $2\text{CaO} \cdot \text{Al}_2\text{O}_3$ in $2\text{CaO} \cdot \text{SiO}_2$.

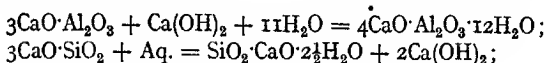
The character of the cement depends on the relative proportions of the two materials and upon the degree of concentration of the solutions of aluminates in the silicate.

These solutions are produced by diffusion at a temperature below the melting-point of the components or of the resulting solid solution (sintering). The rapidity of diffusion is naturally dependent on the temperature, and probably on fineness of grinding.

Setting and Hardening.—In the main Le Chatelier's theory is generally accepted. The process is essentially one of hydration. The aluminates and silicates first take up water and then undergo hydrolysis, calcium hydrate being set free, and a solid residue of less basic hydrated aluminates and silicate remaining. The aluminates react most readily with water and bring about the initial set. The silicates react more slowly after setting has occurred. In either case the aluminate or silicate dissolves in the water, first integrally, producing an unstable solution which becomes saturated in the neighbourhood of the solid. Hydrolysis then takes place, and the $\text{Ca}(\text{OH})_2$ set free being in excess of that necessary to form a saturated solution, a portion crystallises out. Le Chatelier stated originally that the following hydrated salts were the only ones capable of existing in the presence of excess of lime—



and that these salts are decomposed in the presence of a large excess of water, liberating lime. The reactions were represented by the equations—

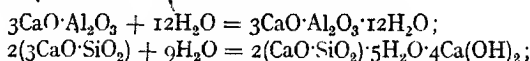


the first equation representing the setting and the second the hardening process.

More recently, however, Candlot proved that the exact formula of the hydrated aluminate in set cement is $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$, and therefore that it is formed by direct hydration of the

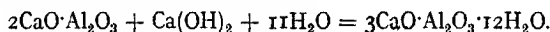
tricalcium aluminate, and not with the addition of lime. Le Chatelier has come to the conclusion that calcium ferrite has the same composition as the aluminate.

Le Chatelier's theory may therefore be summarised in the two equations—



the initial set being due to the aluminate which hydrates and hardens like plaster, and the later hardening being due to the decomposition of the tricalcium silicate giving microscopic needles of mono-calcic silicate (hydrated) and large hexagonal plates of $\text{Ca}(\text{OH})_2$.

Assuming Candlot's formula for the hydrated aluminate to be correct, and that, according to Newberry, the dicalcium aluminate is present in Portland-cement clinker, a possible representation of the setting process is—



The hydration of dicalcium aluminate has not been completely studied.

If we accept the physico-chemical view of Richardson and Rohland, the above explanation only requires slight modification.

The stable equilibrium of the solid solution is upset by the addition of water and free lime is liberated, the aluminate being first decomposed. The water quickly becomes supersaturated with $\text{Ca}(\text{OH})_2$, and the latter crystallises in a network of crystals which binds the particles of undecomposed Portland cement together. The initial set is due to the more rapid crystallisation of $\text{Ca}(\text{OH})_2$ from the aluminates. Subsequent hardening is due to the slower liberation of lime from the silicates. If the lime is liberated more rapidly than it is possible for it to crystallise out from the water, expansion ensues, and the cement is not volume constant. Most of the lime needed for the setting is furnished by the alite, the celite being stable in water.

The strength of Portland cement after setting is due entirely to the crystallisation of $\text{Ca}(\text{OH})_2$ under certain favourable conditions, and not at all to the hydration of the silicates or the aluminates, since in this act of hydration nothing can take place which would tend to bind these silicates and aluminates together.

As celite ($2\text{CaO}\cdot\text{SiO}_2 + 2\text{CaO}\cdot\text{Al}_2\text{O}_3$) is only decomposed slightly in water, it should follow that the strongest cement

corresponds to a minimum of celite or a maximum of alite. This is confirmed by experience—i. e. high lime cements, if thoroughly burnt, are strong.

This view differs from Le Chatelier's in that it considers setting as due indirectly to the presence of silicate and aluminates.

According to Richardson, when celite is rich in aluminate, the cement is quick-setting. The rate of cooling probably affects the amount of celite formed. Increased amount of celite decreases "volume constancy." Since dicalcium aluminate lacks this property, Richardson has made cements in which Al is replaced by Fe and Mn, Ca by Ba and Sr., SiO_2 by P_2O_5 , etc. These cements were, however, not always volume constant. Industrially, the experiments are interesting in so far as they point to the fact that it might be possible to make a Portland-cement clinker, at a comparatively low temperature, from a siliceous ore of iron and a pure limestone.

Richardson points out that fineness of grinding of the raw materials is accompanied by saving of fuel, and also in time necessary for exposure to a definite temperature.

Unsoundness is generally attributed to free lime. Any lime not held in combination with SiO_2 and Al_2O_3 (or in solid solution) behaves like a sluggish quicklime, hydrating to an amorphous product undergoing the mechanical process of apparent expansion and bringing about cracking.

Some people think that free lime is impossible in cement. Expansion is attributed to the formation of a "vitreous, unstable, high-lime compound," which hydrates so slowly that it may be months before visible hydration even commences; but the hydration is accompanied by enormous expansion.

Hydration, Hardening and Setting of Cement.—Paul Rohland¹ asserts that hydration reactions, whether organic or inorganic, take place spontaneously, and their velocity is very much affected by small quantities of foreign substances and by temperature. Hardening does not always accompany hydration (e. g. quicklime falls to powder); it is, therefore, due to some special circumstance. The author believes that a solid solution is formed in all cases in which hardening accompanies hydration. The catalytic acceleration or retardation of hydration by salts is regarded as a result of a change of the solubility of the solid substance which is undergoing hydration.

E. Jordis² adversely criticises the views of Rohland regarding

¹ *Zeit. Elektrochem.*, 1904, 893–900.

² *Ibid.*, 1904, 938–940.

solution for 29 and 186 days, gave residues approaching the composition $3\text{CaO}\cdot\text{SiO}_2\cdot 3\text{H}_2\text{O}$ and $3\text{CaO}\cdot\text{SiO}_2\cdot 6\text{H}_2\text{O}$.

It will be seen from these excerpts that opinion has fluctuated a good deal, and again, I have to thank Mr. Alderton for his care in preparing another set of notes in 1910, which are appended. References are given in the more important cases.

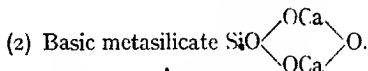
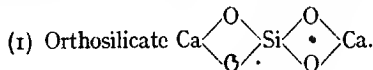
SUMMARY OF SOME RECENT VIEWS ON CHEMISTRY OF PORTLAND CEMENT (1910)

Alumina with silica, lime, and magnesia, binary systems of:—
E. S. Shepherd, G. A. Rankin, and F. E. Wright.¹

In addition to experiments with the lime-silica series of minerals, an investigation has now been made of the alumina-silica, alumina-lime and alumina-magnesia series. In the alumina-silica series only one compound, $\text{Al}_2\text{O}_3\cdot\text{SiO}_2$, was found to be stable in contact with the melt, the optical properties agreeing with those of the mineral sillimanite. The two other minerals, cyanite and andalusite, which have the same composition, slowly change into sillimanite at temperatures above 1300°C . There are four definite compounds of lime and alumina, $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$, m.-pt. 1337°C .; $\text{CaO}\cdot\text{Al}_2\text{O}_3$, m.-pt. 1587°C .; and two with no definite melting-point, $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ and $3\text{CaO}\cdot 5\text{Al}_2\text{O}_3$, but which are completely melted at 1550° and 1725°C . respectively. It is considered probable that only the compound, $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, occurs in Portland cement. There is only one compound of magnesia and alumina, $\text{MgO}\cdot\text{Al}_2\text{O}_3$, similar to the lime-alumina compound. The temperature range of the lime-magnesia system is too high for satisfactory investigation, but it is considered to be an eutectic series, with no compounds and little of any solid solution. A detailed description is given of the optical character of the various products, together with a number of tables and curves.

Zulkowski says that tricalcium silicate does not exist.

Dicalcium silicate exists in two modifications—



¹ *Amer. Jour. Science*, 1909, 28, 203-333.

The latter only has hydraulic properties: it is the more stable variety at high temperature, and is retained by sudden cooling. With slow cooling there is formed a mixture of the two isomorphous silicates. The presence of the orthosilicate gives a tendency to disintegration in the Portland cement.

Portland cement contains therefore, dicalcium silicate and dicalcium aluminate and free lime. The function of the latter is merely to keep the absorbed water alkaline and so facilitate hardening.

The above view also applies to slag cement: high lime slags, when slowly cooled, tend to disintegrate: when suddenly cooled they possess hydraulic properties.¹

Michaelis agrees with Day and Shepherd that calcium orthosilicate ($2\text{CaO}\cdot\text{SiO}_2$) is the principal constituent of Portland cement. Tricalcium silicate is a solid solution of CaO in $2\text{CaO}\cdot\text{SiO}_2$. Alite is a mixture of calcium orthosilicate, dicalcium aluminate, and lime in solid solution, which can vary within wide limits. Its constitution is not, however, certain. He accepts Day and Shepherd's three modifications (α , β and γ) of dicalcium silicate. The change from the α to β occurs at 1410°C ., and β to γ at 675°C .

The solid solution of lime gives the crystals a tendency to "break up." By the action of water a great part, even more than the total dissolved free lime, separates as hydrate. When kept at a red heat, and even by lengthy warehousing, the dissolved lime separates more or less: the solid solution dissociates.

Al_2O_3 and Fe_2O_3 can replace each other only to a certain extent. There is no Fe_2O_3 , "Alite." Calcium ferrite will not crystallise alone or with $2\text{CaO}\cdot\text{SiO}_2$. The mixture of $2\text{CaO}\cdot\text{SiO}_2$, calcium ferrite, and lime is equivalent to "Celite," in which the ferrite exists as an undissolved magma.

Regarding slags, those which contain a large proportion of orthosilicate fall to powder owing to change into the γ modification (at 675°C). So do Portland cements which are either poor in lime or which have been kept too long at the glowing temperature, and so allow the solution of lime in orthosilicate to dissociate and so form free orthosilicate which can then change into the γ form.

Michaelis, in agreement with Zulkowski, notes the beneficial effect of the alkalinity of the water in setting and hardening. Slags can be so treated, however, that they require no addition

¹ *J. S. C. I.*, 1907, p. 925.

of free lime, but harden straightway with water. This is effected by Passow's process. A part of the slag is cooled for a sufficient time at $900-700^{\circ}\text{C.}$: the gehlenite ($2\text{SiO}_2\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaO}$) splits up into anorthite ($2\text{SiO}_2\cdot\text{Al}_2\text{O}_3\cdot\text{CaO}$) and free lime, and the CaS partly converted to CaSO_4 and free lime (with evolution of SO_2). The slag then becomes "spongy" and contains free lime.

Passow mixes 60 % glassy slag and 40 % spongy slag, the free lime in the latter being sufficient to effect the hardening of the whole mass. Michaelis says that freshly-prepared Passow cement (made by the older process—*i. e.* without Portland cement addition) makes good mortar, but will not keep, owing to finely-divided free lime being converted to CaCO_3 . Passow has therefore found a more stable source of lime in Portland cement, 15-25 % of which he adds to the slag. The free lime formed by the hardening of the Portland cement is utilised to harden the slag.

Schott¹ thinks that Portland cement does not contain tricalcium silicate. His view is that Portland cement is a solution of lime in dicalcium silicate. The hydraulic properties increase with the amount of lime in solid solution. Dicalcium silicate, however, cannot dissolve more than a half equivalent of CaO. Any lime in excess of this exists in another condition—free lime. The same considerations apply to dicalcium aluminate. Portland cement is therefore a solution of CaO in $2\text{CaO}\cdot\text{SiO}_2$ and $2\text{CaO}\cdot\text{Al}_2\text{O}_3$, the amount of lime in solution depending on the raw materials, but must not exceed that required by formula $5\text{CaO}\cdot 2\text{SiO}_2$ and $5\text{CaO}\cdot 2\text{Al}_2\text{O}_3$.

It is also possible that a double compound of $2\text{CaO}\cdot\text{SiO}_2$ and $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ is present in which lime is held in solid solution. Certain experimental results of the author favoured the latter theory.

Rohland considers that the tricalcium silicate of Le Chatelier and Newberry is a solid solution of lime in a less basic silicate, and that the hydration of Portland cement is a simple hydration of the less basic silicate and of the free lime.

Meyer says that tricalcium silicate is the essential constituent of Portland cement, and that other minerals present are—

- (1) Isomorphous mixture of $3\text{CaO}\cdot\text{SiO}_2$ and $2\text{CaO}\cdot\text{SiO}_2$.
- (2) Silico aluminate of lime.
- (3) An aluminate of lime present in badly-burnt cements

¹ Calcium silicate and aluminate in relation to Portland cement (19c)

Aluminium Calcium Silicates.—A systematic investigation of the fusibility of aluminium calcium silicates has been made and the results plotted as a triangular diagram. The surface of fusibility presents two maxima at 1500°C. and 1510°C. respectively, corresponding with the silicates— $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ and $8\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$. The first is regarded as a definite chemical compound, since its polished surface, washed with 10 % HCl and examined microscopically, exhibits almost complete homogeneity. Further, analyses of crystals separated by hand or by washing with methylene iodide gave results closely approximating to the above formula.

The Micrography of Cement.—E. Stern has introduced the micrographic method of examination by reflected light, as used for testing alloys, for the purpose of examining set cements. The normal structure of hardened cement consists of two kinds of constituents: A primary and B secondary. Constituent A is practically the unaltered cement grain, whilst the B constituent represents the products of setting and hardening. The micrographic picture may be measured by the planimeter, and the relative proportion of A and B thus estimated. The structure remains practically unaltered during setting and hardening, although the very prolonged action of water gradually increases the proportion of B at the expense of A.

By etching the cement surface the A constituent may be further resolved, and the resistant grains of the hardened cement are then seen to consist mainly of alite. Suitable etching agents are alcoholic HCl, alcoholic iodine, and 25 % HF. The method shows a very distinct difference between the normal structure of ferruginous cements and ordinary Portland cements; by etching with HF the particles of slag may be recognised in the former by brilliant interference colours, and their proportions approximately estimated. Sea water modifies the appearance of the structure of sections of cement in a different manner from fresh water. A 1-2 % solution MgSO_4 acts similarly to sea water. When the hardened cement is subjected to high temperature, the structure becomes less distinct the higher the temperature, and the B constituents lose their water of combination and shrink together. With regard to the processes of setting and hardening, micrography shows that the setting process probably consists in the formation round each particle of a relatively very narrow zone of hydration products.

With this the formation of structure constituents is apparently

CEMENT

at an end, and all further changes (hardening) which take place inside the B constituents cannot be followed micrographically, because B appears to be a uniform substance by reflected light. The micrographic study of synthetic products will facilitate research on the physical (temperature) and chemical (composition) conditions necessary for the production of cement.

There are various other papers which are in my hands, but appear to me too indefinite to need more than citation. The chief of these are by Schott and Zulkowski. It must not be supposed that such papers should be dismissed without consideration. They must be studied by every chemist who wishes to have a knowledge of the stages of thought through which this very difficult branch of science has passed or is passing.

Before I sum up I should like to refer the readers of this book to the very thoughtful work of Dr. Desch, which contains numerous photomicrographs as well as a good discussion of theories current at the time the book was written.

I must now, as it were, go into the witness-box myself, and say what I believe is the present state of knowledge. Certainly Portland cement is made in commerce by combining SiO_2 and CaO by the aid of some flux which may vary from Al_2O_3 to CaCl_2 . The product of chief significance is $3\text{CaO} \cdot \text{SiO}_2$. Its mode of setting is a matter of debate, but it is difficult to accept the theory of a "gel," although it is attractive. I find no evidence of the existence of a "gel" of such mechanical strength as will account for the great mechanical strength of Portland cement. On the other hand, I find no direct evidence of the supersaturation of water by tricalcium silicate or its products, its deposition, and again the supersaturation of the water. Balancing all the facts within my knowledge, I prefer the crystalline theory. And here it is right to say that although photomicrography has been freely used by various competent observers, it has taught us little of a positive kind. Experience has shown that photomicrographs of clinker are comparatively easy to prepare, but their interpretation is very difficult. The preparation of photomicrographs of set cement is very difficult and usually baffles the best petrologist. With some practice in the art of cutting sections of comparatively soft material, I have failed consistently, and equal lack of success has attended the efforts of those professional section cutters whom I have employed. A good many photomicrographs of clinker and of set cement have been

published, but are not reproduced here, as their accuracy is so doubtful and their interpretation so imaginative that they are more likely to confuse the inquirer than to help him.

Before dismissing the question of the photomicrography of cement the essence of an interesting article by E. Stern,¹ quoted above, may be referred to. Evidently the writer has found the same difficulty as his colleagues, and wisely comes to the conclusion that contemporary knowledge is insufficient. He has tried a new method—that is, to use *reflected* light instead of *transmitted* light, generally employed for thin and transparent specimens. To do this is difficult enough, even, with a metal if it is as soft as lead or thallium, and, in fact, can scarcely be accomplished save by squeezing the metal on a microscopic slide; it is practically impossible for examining a substance which, if similarly squeezed, would lose all its characteristics. It is clear that some better micrographical method must be found before a tolerable section can be had for examination by reflected light.

In short, the *chemistry* of Portland cement, as distinct from its ultimate analysis, is in a state of flux, and will remain so until far more thorough and difficult researches are made than those extant.

¹ Ber. 1908.

CHAPTER X

THE FUNCTION OF THE VARIOUS CONSTITUENTS OF CEMENT

IN previous parts of this book reference has been made to the nature of the various constituents of cement, which have been described in their proper place.

Their function is not yet completely known, but, having regard to extant knowledge, it may fairly be said that the primary action of the higher silicates is hardening, and the primary action of the aluminates is setting. There has been much controversy on these subjects, and a great deal of pseudo-science has been lavished in maintaining untenable theories. Without *parti pris* it may be said that the least defensible propositions have originated in the United States of America.

I have endeavoured to give an impartial account of all hypotheses which are worthy of serious attention, and to the best of my ability have summed these up and appended my personal view. According to that—it must be understood that this may be regarded as a corollary—I am, as concerns the colloid and crystalline theory, much in the position of the historical donkey between two bundles of hay. But although there is no doubt that there are various constituents in cement, each of which has as its province a fundamental influence both on the setting and on the ultimate strength of the cement, it is still a matter of debate what these are and what province they occupy. I wish to emphasise this because, hazed by the “phase rule,” many eminent chemico-physicists have pretended—using that word in its right sense—to solve the whole problem. It comes to this, that at the present date all hypotheses concerning the functions of the various constituents of cement, though definite enough, are not definitive.

To come to positive ground. Our knowledge at present is empirical—that is to say, it rests upon experiment and also on experience, and this concerns not only the chemist but also the user of cement. The simplest case may be taken first; cement, being a basic substance, is readily attackable by all

acids, including carbonic acid. As carbonic acid is a normal constituent of the air and of natural waters, whether fresh water or sea water, it follows that cement exposed to any of these will be attacked, particularly when the carbonic acid from these sources can obtain free access to the cement. Fortunately, as cement when set contains a large quantity of calcium hydroxide, carbonic acid combining with the calcium hydroxide will form a seal, filling the interstices of the work and making it impervious. The process is precisely analogous to the hardening of ordinary lime mortar, and unless there is something external to the cement work which will attack this calcium carbonate, the cement structure will be permanent. It is true that carbonic acid itself will attack the calcium carbonate which it has formed and dissolve it, but if the face of the work presents few rugosities the attack will be so slow that the term "permanent" used above may be regarded as almost exact.

It is very different when the work is porous, and particularly so when it is subject not to fairly quiescent media such as still water containing carbonic acid, but to media flowing to and fro, and so providing new supplies of carbonic acid for solution of the protective coating of calcium carbonate. The situation becomes acute when the attacking agent is not carbonic acid but any salt which has a chemical action of a more vigorous kind on the calcium hydroxide inevitably produced in the setting of cement. The commonest example is the magnesium salts present in all sea water, and this, in a subsequent paragraph, will be dealt with more fully. In the present place it is sufficient to say that of the various constituents of cement the most sensitive to attacking substances is calcium aluminate.

CHAPTER XI

USES OF CEMENT

WITH regard to the uses of cement, their name is legion, ranging from the filling of ships intended to be scuttled to elegant and even ornamental structures, vying with masonry recognised as architecturally beautiful. The fundamental difficulty in making a really fine building of cement is that this has to be put in in a plastic state and allowed to set, and, when it has set, it is not as a rule beautified by carving. In fact, a structure made in cement presents very much the same differences as between metal casting and the same metal chased. But just as modern methods of casting will give replicas of the design so sharp that with the merest trimming up they are almost as expressive of the meaning of the artist as the carved work which came from his hand, so the modern methods of moulding cement approach a similar degree of success. Nor has the art of preparing a beautiful structure in cement been by any means pushed to its limit—such things as balustrades, cornices and whole façades can be prepared with a surface so well finished that when the structure is regarded as a whole, the effect is entirely acceptable. The natural course is to line the moulds with a thin layer of much finer and better cement, filling in in the ordinary way with sound concrete not too coarse, so that the finished structure may present a face comparable with that of worked stone. Nor is there anything sham or inartistic in this; everybody knows that many modern buildings have a steel skeleton, and are faced with some appropriate material; the result is handsome.

As to the material for facing such castings in cement, it may be of any colour, including white. Obviously a plaster face would be useless for exposed work, and even if not exposed would act on the cement if moisture obtained access to the two materials. But true Portland cement, almost chemically free from iron and manganese, is white, and, a more agreeable white than the cold and dazzling white of chalk, whether used as such or in the form

of plaster. It will be seen from this that the one obvious limitation to the use of cement in buildings of architectural pretensions is often much exaggerated, and in point of fact arises chiefly from ancient prejudice in favour of stone dating back to the time when architects were both builders and masons. Most stones, except basalt and granite, are only sub-permanent, and when disfigured by decay and grime have an attractiveness which is subjective. In short, a spectator regards them entirely conventionally, just as he would prefer a concrete structure if he had been brought up to believe in it. It must be quite understood that these remarks do not refer to cases where the facing is definitely a sham and serves no purpose whatever. The most notorious instance is the Tower Bridge, which is plastered with pieces of stone concealing its essential beauty of structure, and which are of about as much use as layers of wadding padding Apollo. Throughout all ages, the largest and oldest use of cement of all kinds has been for heavy structural work, and every grade of cement has been employed, ranging from the hydraulic lime used by the Romans for their bridges, aqueducts and sewers, to harbour works of the most recent date made of modern Portland cement. For harbour work a good deal of doubt existed as to the permanence of cement, thoroughly justified by the comparatively poor quality of cement made fifty years ago, and by a want of comprehension of the best mode of using it. All this is changed now, and unless some unusual local condition prevails, it may safely be said that all harbour work is carried out in this material with a certainty of success in construction and permanence. In the early days of railway work, brick and stone were freely employed for bridges and viaducts, and as in this country the railway system was fairly complete before engineers felt fully confident of its stability, there is less structural work in Portland cement than might be expected in the country of its origin. But there is a great deal for all that, and when new lines are made, doubtless it will replace stone and brick wherever its cost is lower. In the same way the older form of sewerage systems in brick set first in mortar, and later in cement mortar, is being replaced by concrete, and the subsidiary structures, such as settling tanks, bacterial beds, necessary for the treatment of the sewage, are also made in concrete. The same remark applies to waterworks, whether for town supply or for power. Generally speaking, except where very heavy heads have to be handled, concrete conduits are perfectly satis-

factory, and probably the limit is not reached yet, and will be approached when reinforced concrete is more generally adopted.

• An excellent example of the use of concrete is afforded by the rectangular conduit at the British Aluminium Company's Power Station at Kinlochleven. This channel, which is reinforced by expanded metal and is covered to prevent it being blocked by material brought down from the side of the hills by streams when in spate, follows the contour line and arrives at a point above the power house with but trifling loss of head. The drop to the turbines from this point is so great that steel pipes are necessary, and a battery of these carries the water under high pressure to the power house. It may very well be that reinforced concrete, however good, could not be made to serve for such a heavy pressure, but I see no reason why they should not be used—as probably they are—for smaller heads. Other large uses of cement concrete are for heavy buildings of all kinds, such as granaries, flour mills and warehouses. In granaries this material is particularly useful, as the grain is always handled in bulk, and in this state exercises a quasi-fluid pressure on the walls.

Mills and factories containing heavy machinery demand just those qualities which concrete possesses, and if the "lay out" is properly designed, foundations for the machinery can be put in when the building is constructed, the whole being, in fact, monolithic. There are a host of other uses, such as groynes, piers and piles. It will be realised that in almost all cases what can be done with concrete can be done, and better done, with reinforced concrete. Piles may be taken as an example of a structural member which could not be made in simple concrete, but is made and used with complete success in reinforced concrete.

Formerly piles were moulded vertically, but the modern practice is to form them horizontally. A trough of wood is provided with a steel shoe which is to form the point of the pile at one end, and along the trough are laid steel rods set in from the wood casing sufficiently far to allow concrete to be rammed between them and the wood casing. The concrete, which should have a fine aggregate and be rich in cement, say 1 to 5, is then rammed by hand into the trough. The main members of the reinforcement—that is, the steel rods—are tied together by a stout steel wire so as to make the whole reinforcement rectangular in section, equidistant from all sides of the wooden casing and mechanically strong. The filling up of the horizontal box con-

taining the steel skeleton, uniformly surrounded and filled with concrete, proceeds continuously until the pile is complete, when the whole is allowed to set. When it is sufficiently matured it may be freely handled like any other structural unit, transported into place and driven. As direct blows with the pile-driver on the top of the pile might crack or spread the head of the pile, it is usual to protect the head with a removable steel cap having a packing of sawdust, sacking and the like inside. The driving then presents no difficulty, the pile descends to the depth required and the head remains uninjured; if cracking occurs, the head of the pile can be cut off, the concrete being chipped away and the metal cut through by an oxyacetylene blowpipe. There are certain questions as to the stability of these piles, especially in sea water, and particularly between wind and water. These are simply special cases of the general question of the stability of concrete; perhaps I may be allowed to quote from a paper which I presented to the International Engineering Congress, and read before that body at San Francisco in 1915.

"The quality of cement for reinforced concrete must be at least as good as that for ordinary concrete, and, if possible, should be better. This is not because the latter should not be as near perfection as the maker can achieve, but because Portland cement for reinforced concrete is, as it were, a pioneer of progress, and what is a special brand for such purposes to-day will be the ordinary commercial article to-morrow. Turning to steel, as the other partner of the association, one may say that no better example of the advantage of that scientific direction which is now applied to Portland cement could be found than in the case of the steel, and it is significant that the metal, the more difficult of the two to manufacture, was being made of good and uniform quality before chemical principles were recognised and acted on in the manufacture of Portland cement. Thanks to the fact that for some forty years the regulation of the composition has been in the hands of the chemist, little is left to be desired in the modern commercial product. Of course, cases have occurred, and will occur, of careless manufacture and inspection where brittle and inferior material has found its way into the work, but they are not numerous and only rank with such failures as arise in all structures. Good as modern mild steel is, it may be properly asked whether, in some cases at least, steel of a higher grade and greater tensile strength may

be advantageously used, and I think that most of us will assent to this. This applies to ordinary structures, and is, of course, obligatory for such buildings as safe deposits, where the metal must not only have a good tensile strength but be so hard as to be practically undrillable.

"I began this paper, by saying that there is no such thing as a permanent structure, and I end by stating that in my opinion a pyramid, a bridge, an aqueduct, a harbour, a coliseum or a cathedral made in concrete or ferro-concrete, well and honestly enough, will vie in life with the mighty structures of antiquity which are left to us, their limitation of life lying not in themselves, but in the changing needs of human life."

The question of the probable life of reinforced concrete has formed one of the topics of a Committee of the Institution of Civil Engineers, of which the writer has the honour to be a member. At the request of the Committee I contributed a memorandum in February 1910, which runs as follows—

"There are two matters affecting the stability and permanence of reinforced concrete which appear to me to be of special importance.

"The first is the risk of destruction of the cement in the concrete, and of corrosion of the steel constituting the reinforcement; the second, the stresses due to expansion of the concrete and the steel, and to the difference in the value of the coefficient for the two materials.

"The likelihood of the attack of the cement itself depends on the same conditions as determine whether ordinary concrete—unreinforced—is attacked, but as the thickness of the concrete over the reinforcement is usually small, it is evident that even more care must be bestowed on the avoidance of those conditions than in the case of concrete in large masses, where the surface of attack is relatively smaller. With regard to the steel, the risk of corrosion is primarily dependent on the continued access of water to the steel. Mere moisture left in the concrete after its preparation, or any stationary water, is of small consequence, because that water soon becomes saturated with lime and forms an alkaline medium excellently adapted for the preservation of steel. But continued access of water, involving anything approaching a flow of water, will remove this preservative lime, and cause the customary rusting of steel exposed to water. It follows that the concrete of armoured concrete must be practi-

cally impervious. This need for imperviousness, has been recognised in practice by making the concrete rich in cement, but, as far as I know, no measurements of the permeability of the mixtures ordinarily employed have been published. Such experiments as I have carried out have been directed to a different end, and have been made with mixtures of cement and standard sand, and go to show that, though at first pervious, such mixtures soon become moderately watertight. Similar experiments with concrete composed of cement, sand, and small stones, such as is ordinarily used for reinforced concrete, would be useful. Imperviousness of reinforced concrete, while desirable in all cases, becomes of great importance in structures immersed in fresh water, and imperative for those in sea water.

"The coefficient of expansion by heat of mild steel is well known, the figures generally accepted being 0.0000069 per degree F. That of concrete varies somewhat with the composition, but for a 1:2:4 mixture is usually taken at 0.0000055 per degree F. For a mixture of one of Portland cement to one of sand, I have found 0.0000053 per degree F. wet and 0.0000073 per degree F. dry. These values are so similar that the stresses resulting from their difference are small. But the stresses due to the two materials regarded as a whole in a structure hindered from expansion may be considerable, and should certainly be computed in cases where the structure is exposed to a large range of temperature. Further, there are no data (so far as I have been able to ascertain) concerning the alteration of length of concrete which takes place by alteration of wetness and dryness. If this, as seems probable, is considerable, serious stresses may arise, both in a structure not free to expand and between the concrete and its reinforcement. Experimental investigation of this question appears to me to be desirable.

"From what has gone before the general utility of cement will be understood, but there are a few special instances which may be cited. A brick chimney is costly and troublesome to erect, whereas one made of reinforced concrete could be put up in about half the time, being built much in the manner of a hollow pile. The lower part of the chimney would, of course, be lined with firebrick precisely as in the case of a brick chimney, but as soon as the gases are cooled to about 150° C., the concrete will stand it, and provided that no condensation occurs of the water in the flue gases there will be little or no attack by the oxides of sulphur present in the flue gases. Another

Instance of pressing importance is the use of concrete for building ships, already alluded to in the preamble of this chapter, and examples of this sort might be multiplied indefinitely. In short, wherever a material, high in tensile and compressive strength, and one which can be moulded into any required shape almost as easily as cast iron is run, is needed, then concrete, of proper composition for its determined purpose, may be used; further, it cannot be too much insisted on that such structures are cheap, because the essential ingredient (cement) forms but a small part of the total weight of the structure. I would not endorse the statement of the grandfather of one of Stevenson's characters (Lowden Dodd), 'that Portland cement properly sanded will go a long way.' Modern tendency is altogether in the other direction: good cement 'properly sanded' will go a long way, but the engineer knows that if he makes an error it is better to err on the side of richness."

CHAPTER XII

EFFECT OF VARIOUS SUBSTANCES ON CEMENT

ACTION OF SEA WATER

THERE are various materials which, by themselves or used as an aggregate for cement, are destructive thereto. The commonest and most important is sea water. It is well known by harbour engineers that their concrete blocks or cement put *in situ* will ultimately perish. Many experiments on this point have been made: as far as I know, few have been carried out in this country, but French and Scandinavian engineers have put down blocks of concrete in the tideway at different points on their coasts and have observed them over a long series of years. Barring such accidents as have happened from storms and the like, the consensus of opinion is that these blocks are doomed to destruction. It by no means follows that a structure such as a harbour will be destroyed in a short time. Personally, I believe that a harbour properly built will last as long as there is any need for it. Long before it has been destroyed by the action of sea water the utility of the harbour will have disappeared.

The action of sea water on cement, apart from any erosive effect, is to replace calcium salts by magnesium salts naturally present in sea water. The magnesia of the latter salts has no cementitious value, and the calcium salts go into the sea water, with the result that the cement has no strength, and, in fact, perishes. Many such cases are well known, and, within my own recollection, have led to grave mistakes. Accurate analyses were made, showing that the damaged cement contained large quantities of magnesia. The deduction which was made was false: it was that the magnesia came from the cement, whereas, of course, it came from the sea water which had attacked the cement. This led to the erroneous belief that magnesia in cement was pernicious. This view was buttressed by similar accidents on the Continent, some of which had nothing to do with sea water.

The leading case is afforded by Stefans Dom in Vienna, which went to pieces, and on analysis was found to contain a good deal of magnesia. The chemist of that date (about 1890) regarded the magnesia as the *foens et origo*. There is no evidence of any sort that this is the truth. The limit of magnesia in true Portland Cement consistent with safety has never been fixed, but to be on the safe side the British Engineering Standards Association have put the maximum percentage at 3 %. It must not be supposed that this is a real limit; it has been adopted purely for security, and with cements of a different class, such as the Rosendale cement of Pennsylvania, is enormously exceeded.

From what has gone before it will be understood that the corrosive action of sea water will be much increased if it can go in and out by the movement of the water, and especially if the tides carry from the concrete the essential calcium salts of the cement and leave behind it worthless un cementitious stuff.

But there is another constituent in sea water to be considered, which is calcium sulphate. It is irrefutable that calcium sulphate will selectively attack calcium aluminates and form compounds of these, whose volume is much larger than that of their constituents, with the consequence that the structure falls to pieces. The remedy is obvious: to prepare cement containing as small a quantity as possible of alumina. It is for this reason that the famous Chaux de Teil has proved itself seaworthy. There are cements in this country and in Russia in Novo Roesick, and no doubt elsewhere, which have the same excellent quality, and attempts have been made in Germany at the Hemmoor Works near Hamburg to prepare cement in which ferric oxide replaces alumina oxide, always with the idea to avoid the action of sea water on calcium aluminates. The consensus of opinion is that it is better to make the concrete itself water-tight, or, if a relatively porous mixture is used for the main structure, to face it with granite rocks, than to seek for a cement unattackable by sea water.

Before leaving this section of the matter, the use of puzzolana should be mentioned. It has been spoken of in some detail in a preceding chapter, but, as far as we are concerned with it at present, it may be said that its function is to combine with the calcium hydroxide set free in the normal setting of Portland cement, and thus absorb and utilise the pabulum on which the magnesium salts in sea water would feed. These things are of practical moment, and the use of puzzolana as an addition to cement

has an important bearing on the stability of all structures especially those exposed to sea water.

I have endeavoured repeatedly, knowing, as I do the value of this material, to induce engineers to employ puzzolana for the heaviest type of work, and have consistently failed. The primary reason is ignorance of the properties of this material, and, secondarily, the difficulty of procuring it in adequate quantities from places as far apart as the Rhine and Java. Moreover, the trass people do not provide the engineer with what he wants. The trass should be finely ground so that it may be intimately mixed with the cement, with the lime of which it will combine. These conditions are not fulfilled, and it follows that structures made with Portland cement alone contain material which could be utilised by judicious admixture of trass. The blame of this neglect lies fairly equally between the constructional engineer and the purveyor of trass. The engineer does not understand the great value of trass, and the purveyor of trass does not realise that about nine-tenths of his product, as ordinarily sold, is of no more value than so much sand, because it is too coarse; it must be finely ground. There is another aspect which is purely commercial: neither makers nor buyers want to use trass because they are accustomed to sell and use Portland cement; the buyers are suspicious of the makers, who might sell them a better material—cement mixed with trass—under the name of Portland cement. Fortunately, the British Standard Portland Cement Specification has cleared up all these things, and Portland cement when bought by its tests, or on the guarantee of the maker, is Portland cement and nothing else.

But this does not touch the real question, which is the proper use, under its own name, of Portland cement ground finely together with puzzolana. As far as I know, no such product has ever been put on the market, and, to use an expressive vulgarism, it is "up to" our manufacturers to sell this material and to convince harbour engineers that it is the best for the very difficult work which they have to face.

EFFECT OF AGGREGATES

The ordinary aggregate is the local stone, gravel or sand, and, as these usually are siliceous or some form of hard and weathered limestone, they are suitable for making concrete. It is obvious that questions of freight come in, as it is easier to

bring cement to the site than to carry aggregate, however good, from a distance: but sometimes it happens that the local aggregate may have a bad influence on the cement with which it is to be mixed, and difficulties often arise from this cause. In many places where good gravel or limestone is absent, there are quantities of slag, useless as they stand, but conceivably useful as an aggregate. The question then arises, will they injure the cement? Two classes may be named:—The first is ordinary blast-furnace slag. If this is an acid slag containing a large percentage of silica, and practically inert, it may be adopted for use as an aggregate without hesitation; but if the blast-furnace slag is of the basic class—that is to say, contains 40 % to 50 % of lime—the question is more difficult.

Constant confusion arises from this term “basic”—the basic slag I speak of is the slag from blast furnaces running on a burden high in lime; what is generally known by agriculturists as basic slag is the product of steel furnaces lined with basic material such as lime and magnesia and running on phosphoric ores; these two things are totally distinct, but are frequently confused.

These basic blast-furnace slags generally contain a considerable quantity of sulphur in the form of calcium sulphide. Provided that they are properly enclosed in a matrix of cement, that sulphur has little chance to oxidise; but if this aggregate is exposed to moisture and air, calcium sulphate will be formed, attack on the cement will ensue, and destruction of the concrete is certain.

To take the second class of slags, the same sort of difficulty arises. There is an abundance of slag from copper-smelting in South Wales and many other places. It contains a large quantity of ferrous silicate; this is an oxidisable substance, and if by exposure to atmospheric influences it should oxidise, it would disintegrate the concrete of which it forms part. Further, sulphides may be present, and these, oxidising to sulphates, would exercise their usual destructive effect on the concrete. In such matters experience is a great, but not the only guide. The chemical composition of all these slags will provide the expert with valuable data, and on the top of this is observation of the behaviour of such slags lying for years on the tip. It need hardly be said that identity must be established between the slag on the tip and the slag proposed to be used, as smelting methods change and the nature of the slag changes correspondingly.

There is a particular case of aggregate which is often over-

looked. In modern methods of construction it frequently happens that light floors are an important part of the stresses on the structure as a whole, and for this reason breeze has been much favoured. Now, breeze ordinarily contains sulphates, or sulphides which are easily oxidisable to sulphates.

Concrete made with this breeze may be stable, provided it is protected from moisture, but when it is used in exposed positions, or in fact wherever water and air can penetrate, oxidation will occur and the cement will be attacked and ultimately destroyed.

These inconveniences are particularly apt to happen when breeze is used for roofs, unless the roof is so fully protected by asphalt or similar material that no water can reach the breeze-concrete. There will be first, an expansion of the breeze-concrete, next a lifting and probable cracking of any imperfect asphalt covering, and finally the pushing out of the parapets and walls of the roof. I have seen many such cases, and almost without exception they are traceable to the access of water and air to the breeze-concrete. It must not be supposed that every breeze has these inherent defects: sound concrete can be made with breeze, but this is an exceptional case, if the breeze is to be exposed to the action of air and water jointly. In short, no breeze should be used for any constructional purpose, in which there is a possibility of atmospheric attack, until it has been analysed and thoroughly tested. Such devices as cutting chases between an expanding roof and its parapet are mere palliatives, and although sometimes useful as the best way out of a bad job, must be condemned without reservation.

In a previous part of this book the attack of cement by sulphuric acid, produced by the oxidation of sulphuretted hydrogen, particularly in sewerage systems has been dealt with. Generalising, it may be said that any acid material will attack cement, and that the degree and extent of its attack will depend on the nature of the acid and local conditions. Each case must be judged by itself, and anything approaching the nature of a canon is impossible; the one point to be borne in mind being that cement, as a basic substance, is easily destroyed by most acid materials.

As in the setting of cement a large quantity of lime is set free as calcium hydroxide, any saccharine solution will dissolve that lime, forming calcium saccharate, the cement will be attacked, and probably destroyed. There is a case which at first sight

seems to contradict this: in California concrete tanks are used for containing locally grown wines, which contain both acid and sugar. These tanks appear to answer their purpose, and the probable explanation is that they are skinned over by calcium tartrate very much as concrete in ordinary use is skinned over by calcium carbonate. Of course, liquid in these wine tanks is practically quiescent, and the in and out movement of the liquid so often referred to is negligible with such trifling tide action.

Quite another state of things exists when oils come into contact with cement. A number of proprietary materials containing various soaps have been put forward as capable of rendering concrete water-tight, and good results have been obtained from some of these. But oil itself usually has a destructive influence on concrete used in the construction of a tank to contain the oil. The reason for such action is obscure. Assuming that the concrete is fully set and that the cement is completely hydrated, it is difficult to understand how an oil can attack it. It seems hardly provable that the oil can displace water chemically combined with a cement. There remains the suggestion that any acid constituents of the oil will act on the cement in the usual chemical way. If so, it would form a calcium salt of the acid constituent, and serve rather as a preservative than as a destructive agent. A case in point as regards the action of oil is the instance afforded by cotton-seed oil. It has been proved by experiment that concrete is attacked by cotton-seed oil, although cotton-seed oil, from its mode of manufacture, is almost entirely free from free fatty acid; consequently it is impracticable to use concrete tanks for containing this oil.

I have given merely instances of substances likely to come into contact with cement in industrial practice, but with the exception of the case of the oils, which is certainly puzzling, it is sufficient to remember that all acids and salts capable of re-acting with the calcium compounds constituting cement are likely to destroy it unless the product of interaction forms a protective coat. In addition, the product of interaction is itself destructive, and the simplest case which can be cited is that of calcium sulphate, formed, we will say, by the action of the sulphates in sea water on the lime compounds in cement. This mode of attack has been fully dealt with in an earlier chapter.

CHAPTER XIII'

BY-PRODUCTS OF CEMENT

THERE are two by-products of cement, one is the waste heat from the kilns and the other volatilised alkalis. The first is of great importance as the balance of heat going up the chimney is about 30 % of the total fuel burnt in a kiln. The temperature in the burning zone of an ordinary rotatory kiln is not less than 1200° C., and in the case of short kilns, handling dry raw materials, the temperature of the flue gases may be as high as 800° C. When wet raw materials are used the flue gases naturally have a lower temperature, although the number of thermal units contained in them is the same. It follows naturally that it is easier to pick up the waste heat from a dry process plant than from one using wet raw materials. Many attempts have been made to deal with both, but, as far as I know, without practical result. The fundamental reason is that any cement kiln must have an adequate draught, and any apparatus of the economiser type which would provide steam for the general use of the plant would be apt to impair this draught. Further, even if the draught were provided by a fan there would be the difficulty of the dust which comes out at the upper end of all cement kilns, capable of clogging plant of the economiser type. But this loss of heat has appealed so strongly to many inventors that it has been proposed not merely to raise steam by the heat of the gases at a temperature well above boiling-point, but to take the waste gases from such apparatus and to use them in a low-temperature heat engine, employing a fluid such as sulphur dioxide. These attempts have failed for practical reasons. At the normal price of coal it is cheaper to burn a little more fuel than to encumber a simple plant with a number of auxiliary plants somewhat high in capital cost and troublesome and expensive to run.

The simple process of picking up the heat from the waste gases by such a plant as the ordinary regenerator or blast-furnace stove promises little success, as the gases from a cement kiln are not combustible and are too low in temperature. But the idea

must not be lightly dismissed on that account; there is a large and definite amount of waste heat going out from every cement kiln; and as fuel grows dearer it will be more and more worth recovering.

The other by-product from cement manufacture is the flue dust, of which large quantities are produced; naturally, the proportion is larger in the dry process than in the wet, but in either case it is substantial. Regarded originally as a nuisance, this flue dust has shown itself to be of value. To take the first case—that is, the nuisance: I have seen a battery of cement kilns, working on wet raw materials, producing so much dust that the sky was clouded, and family washing in the neighbourhood put out to dry was seriously soiled. I have similarly seen a single cement kiln, working on the dry process, giving out such a quantity of dust that a large house in the neighbourhood had its amenity seriously disturbed when the wind set in its direction. On account of these troubles, rather than with any view of utilising the dust, elaborate methods of catching the dust in a chamber at the base of the chimney-stack, or even by scrubbing the gases, have been employed with success. Of course, both methods have the disadvantage of cooling the exit gases and impairing the draught. The dust has to be removed from time to time from the collecting apparatus, and the natural means of utilising it is to put it back into the raw materials and pass in through the kiln again. This is good as far as it goes, but fairly recently it was found that the dust does not consist merely of the coal ash and the finer particles torn away from the raw materials in the kiln, but is a product of thermo-chemical selection. This fact is, of course, ordinary chemical knowledge, but its practical importance has only lately been understood—a fact somewhat curious, inasmuch as the drying-floors of the old chamber-kilns are always incrustated by a saline deposit. This arises from the alkalis present in cement, and every cement tester knows that the water in the tanks for his test pieces is soft and alkaline. Usually he regards that as coming from the lime in the cement. In this he is mistaken, the alkalinity being due chiefly to alkalis dissolved from the cement. It is usual in cement analyses to return the amount of alkalis by difference, for, as far as we know, these constituents have little or no influence on the quality of the cement, but in the light of the composition of the flue dust, they are worth attention. Under the usual conditions of manufacture the bulk of the alkalis remains in the cement, but a

portion passes through the kiln even in the wet process and appears in the flue dust. As potash in workable quantities is not a common deposit, and, as during the recent war, the chief supply at Stassfurt was inaccessible, much work was done in seeking other sources of this essential substance. The first step was to catch the flue dust from blast furnaces, where the exit gases have a high temperature and contain a proportionately large amount of alkali salts.

Blast-furnace gases have long been used as a fuel under boilers or for internal combustion engines, and in the latter case have to be meticulously scrubbed. But little account was taken of the potash in the dust scrubbed out until potash became a scarce and costly commodity. The next step was to consider the amount of alkalis carried by the flue gases from cement kilns, and in both cases special means of collecting this gas were tried. One of the most promising is the use of high-voltage electricity, which, as is well known, will cause very fine particles suspended in air to congregate into particles sufficiently large to be caught by baffle plates, screens and the like. As in other methods of collecting dust, all these devices have the drawback of requiring that the gases shall be cooled so that the screens can stand the temperature, but this is easily counterbalanced by the value of the potash recovered, the potash being reckoned at its war price. It is a matter for debate whether these processes would pay when the Stassfurt and similar deposits have a world market, but the solid fact remains that the existence of gigantic quantities of a substance absolutely essential for the largest industry in the world—*i. e.* agriculture—have been going to waste since furnaces were first used. So much for the economic side. The technical is easier to pronounce upon. Initially, an attempt should be made to expel the whole of the alkali salts from the raw materials used in any furnace process, without detriment to the primary product. In the blast furnace it may be necessary so to alter the burden as to drive out the alkalis from the slag without detriment to the pig-iron. This is a matter for the chemist and the blast-furnace manager. Much the same thing holds with cement, and the task of the cement manufacturer is more difficult. He cannot raise the temperature of his kiln without going beyond the clinkering-point, and probably burning out the lining of his kiln.

Therefore he must add something to his raw materials which will aid in the expulsion of the alkalis which they contain. On

chemical grounds the most likely substances are the halogen compounds of calcium, but though these have been proposed, I am not aware at the time of writing (1919), that this method has been worked on a large scale with success. Alternatively it has been suggested to increase the quantity of material containing potash by adding to the raw mix such substances as potash felspar. This idea is quite sound, and can be worked in conjunction with the use of halogen calcium compounds as in the previous instance. The cement-maker is in much the same position as the blast-furnace manager in that he has to modify his mixture so as to produce cement of as good quality as before—or better—and this he must consider with a full knowledge of the range of composition of his normal raw materials. For example: if his raw materials are naturally high in alumina, he cannot much increase the percentage of this constituent without injuring the quality of his cement, and he must be cautious in regulating the amount of felspar added. If, on the other hand, his raw materials produce a cement containing a lower percentage of alumina than is usual, he has a freer hand and can add felspar, a material relatively rich in alumina, in greater quantity. Whatever plan is adopted, the whole object is to expel from the highly-heated cement, whether dosed with felspar or not, all the valuable potash which it contains, and to recover this as completely as possible in the flue dust. Like all commercial affairs, these operations come down to a question of cost. It is out of the question to attempt to lay down any rule; the principles enunciated above will hold under all conditions, and the rest depends entirely on the preparation of a proper balance sheet.

APPENDIX I

1920

International Atomic Weights

	Symbol	Atomic weight.		Symbol.	Atomic weight.
Aluminium	Al	27.1	Neodymium	Nd	144.3
Antimony	Sb	120.2	Neon	Ne	20.2
Argon	A	39.9	Nickel	Ni	58.68
Arsenic	As	74.90	Nitron (radium emanation)	Nt	222.4
Barium	Ba	137.37	Nitrogen	N	14.01
Bismuth	Bi	208.0	Osmium	Os	190.9
Boron	B	10.9	Oxygen	O	16.00
Bromine	Br	79.92	Palladium	Pd	106.7
Cadmium	Cd	112.40	Phosphorus	P	31.0
Cesium	Cs	132.81	Platinum	Pt	195.2
Calcium	Ca	40.07	Potassium	K	39.1
Carbon	C	12.00	Praseodymium	Pr	140.9
Cerium	Ce	140.25	Radium	Ra	226.0
Chlorine	Cl	35.46	Rhodium	Rh	102.9
Chromium	Cr	52.0	Rubidium	Rb	85.4
Cobalt	Co	58.97	Ruthenium	Ru	101.7
Columbium	Cb	93.1	Samarium	Sa	150.4
Copper	Cu	63.57	Scandium	Sc	44.1
Dysprosium	Dy	162.5	Selenium	Se	79.2
Erbium	Er	167.7	Silicon	Si	28.3
Europium	Eu	152.0	Silver	Ag	107.8
Fluorine	F	19.0	Sodium	Na	23.0
Gadolinium	Gd	157.3	Strontium	Sr	87.6
Gallium	Ga	70.1	Sulphur	S	32.0
Germanium	Ge	72.5	Tantalum	Ta	181.5
Glucinum	Gl	9.1	Tellurium	Te	127.5
Gold	Au	197.2	Terbium	Tb	159.2
Helium	He	4.00	Thallium	Tl	204.0
Holmium	Ho	163.9	Thorium	Th	232.1
Hydrogen	H	1.008	Thulium	Tm	168.5
Indium	In	114.8	Tin	Sn	118.7
Iodine	I	126.92	Titanium	Ti	48.1
Iridium	Ir	193.1	Tungsten	W	184.0
Iron	Fe	55.84	Uranium	U	238.2
Krypton	Kr	82.92	Vanadium	V	51.0
Lanthanum	La	139.0	Xenon	Xe	130.2
Lead	Pb	207.20	Ytterbium (Neoytterbium)	Yb	173.1
Lithium	Li	6.94	Yttrium	Yt	89.1
Lutecium	Lu	175.0	Zinc	Zn	65.2
Magnesium	Mg	24.32	Zirconium	Zr	90.6
Manganese	Mn	54.9			
Mercury	Hg	200.6			
Molybdenum	Mo	96.0			

APPENDIX II

Useful Factors

From	To	Multiply by
K_2PtCl_6	K_2O	0·19343
K_2PtCl_6	KCl	0·3068
NaCl	Na_2O	0·53027
$Mg_2P_2O_7$	MgO	$\frac{40}{111}$
$Mg_2P_2O_7$	P_2O_5	$\frac{71}{111}$
$Mg_2P_2O_7$	P	$\frac{31}{111}$
$BaSO_4$	SO_3	$\frac{80}{233}$
$BaSO_4$	S	$\frac{32}{233}$
Fe_2O_3	FeO	0·9
Mn_2O_1	MnO	0·93

APPENDIX III

Measures of Length (unit Metre)

Equal to	Inches.	Feet.	Yards.
Millimetre	0·03937	0·003	0·001
Centimetre	0·3937	0·033	0·011
Decimetre	3·93708	0·328	0·109
Metre	39·37079	3·280	1·094
Decametre	393·70790	32·809	10·936
Hectometre	3937·07900	328·090	109·363
Kilometre	39370·79000	3280·899	1093·633

Cubic or Measures of Capacity (unit Litre)

Equal to	Cub. inches.	Cub. feet.	Pints.	Gallons.	Bushels.
Millilitre, or cubic centimetre	0·06103	—	—	—	—
Centilitre (10 cubic centimetres)	0·61027	—	0·018	0·002	—
Decilitre (100 cubic centimetres)	6·10271	0·003	0·176	0·022	0·003
Litre, or cubic decimetre	61·02705	0·035	1·760	0·220	0·027
Decalitre	610·27052	0·353	17·608	2·200	0·275
Hectolitre	6102·70515	3·531	176·077	22·009	2·751
Kilolitre	61027·05152	35·316	1760·773	220·096	27·512

Measures of Weight (unit Gramme)

Equal to	Grains.	Avoir. lb.
Milligramme	0·01543	—
Centigramme	0·15432	—
Decigramme	1·54323	—
Gramme	15·43235	0·002
Decagramme	154·32349	0·022
Hectogramme	1543·23488	0·220
Kilogramme	15432·34880	2·204

APPENDIX IV

USEFUL MEMORANDA

1 oz. troy	=	31.10 grms.	=	480 grs.	=	1.097 oz. avoird.
1 oz. avoird.	=	28.35 „	=	437.5 „	=	0.912 oz. troy.
1 lb. „	=	453.59 „	=	7,000 „	=	16 oz. avoird.
1 lb. troy	=	373.25 „	=	5,760 „	=	12 oz. troy.
1 cwt.	=	50.80 kilos.				
1 ton	=	1016.00 „				
1 cm. sq.	=	0.155 sq. in.				
1 pint	=	34.66 cu. in.				

lbs. per square inch to kilos per square centimetre \times by 0.07031.
 Kilos per square centimetre to lbs. per square inch \times by 14.223.

Area of disc = square of diam. \times by 0.79.

Area of sphere = square of diam. \times by 3.14.

Area of cylinder = diam. \times by 3.14 \times by length.

Solid contents of sphere = one-sixth of the cube of the diam.
 \times by 3.14.

Solid contents of cylinder = square of diam. \times by length \times
 by 0.79.

Holes per square inch to holes per square centimetre \times by 0.155.

APPENDIX V

FOREIGN SPECIFICATIONS FOR PORTLAND CEMENT

THERE are various foreign Specifications for Portland cement intended to attain the same end as that of the British Standard Specification, namely, to procure a cement which shall be a reliable structural material. Naturally they differ a little, partly from local circumstances and partly from the stage of precision to which the testing of cement has been brought in each country. On this account no International Specification has been framed, nor is likely to be framed, but it may be said impartially that a cement which passes the British Standard Specification is as least as good as that acceptable under any of the foreign specifications.

American	Italian
French	Russian
Argentine	

AMERICAN SOCIETY FOR TESTING MATERIALS

STANDARD SPECIFICATIONS AND TESTS FOR PORTLAND CEMENT

Definition.

(1) Portland cement is the product obtained by finely pulverising clinker produced by calcining to incipient fusion an intimate and properly proportioned mixture of argillaceous and calcareous materials, with no additions subsequent to calcination, excepting water and calcined or uncalcined gypsum.

I. CHEMICAL PROPERTIES

Chemical Limits.

(2) The following limits shall not be exceeded :

	Per cent.
Loss on ignition : • . . .	4'00
Insoluble residue	0'85
Sulphuric anhydride (SO ₃) . . .	2'00
Magnesia (MgO)	5'00

APPENDIX

II. PHYSICAL PROPERTIES

Specific Gravity.

(3) The specific gravity of cement shall be not less than 3.10 (or for white Portland cement). Should the test of cement as received fall below this requirement, a second test may be made upon an ignited sample. The specific gravity test will not be made unless specifically ordered.

Fineness.

(4) The residue on a standard No. 200 sieve shall not exceed 22 % by weight.

Soundness.

(5) A pat of neat cement shall remain firm and hard, and show no signs of distortion, cracking, checking, or disintegration in the steam test for soundness.

Time of Setting.

(6) The cement shall not develop initial set in less than 45 minutes when the Vicat needle is used, or 60 minutes when the Gillmore needle is used. Final set shall be attained within 10 hours.

Tensile Strength.

(7) The average tensile strength in pounds per square inch of not less than three standard mortar briquettes (see sec. 51) composed of one part cement and three parts standard sand, by weight, shall be equal to or higher than the following—

Age at test : days.	Storage of Briquettes	Tensile strength : pounds per square inch.
7	1 day in moist air, 6 days in water.	200
28	1 day in moist air, 27 days in water.	300

(8) The average tensile strength of standard mortar at 28 days shall be higher than the strength at 7 days.

III. PACKAGES, MARKING, AND STORAGE

Packages and Marking.

(9) The cement shall be delivered in suitable bags or barrels with the brand and name of the manufacturer plainly marked thereon, unless shipped in bulk. A bag shall contain 94 pounds net. A barrel shall contain 376 pounds net.

Storage.

(10) The cement shall be stored in such a manner as to permit easy access for proper inspection and identification of each shipment, and in a suitable weather-tight building which will protect the cement from dampness.

IV. INSPECTION

(11) Every facility shall be provided the purchaser for careful sampling and inspection at either the mill or at the site of the work, as may be specified by the purchaser. At least 10 days from the time of sampling shall be allowed for the completion of the 7 day test, and at least 31 days shall be allowed for the completion of the 28-day test. The cement shall be tested in accordance with the methods hereinafter prescribed. The 28-day test shall be waived only when specifically so ordered.

V. REJECTION

(12) The cement may be rejected if it fails to meet any of the requirements of these specifications.

(13) Cement shall not be rejected on account of failure to meet the fineness requirement if upon re-test after drying at 100° C. for one hour it meets this requirement.

(14) Cement failing to meet the test for soundness in steam may be accepted if it passes a re-test using a new sample at any time within 28 days thereafter.

(15) Packages varying more than 5 % from the specified weight may be rejected; and if the average weight of packages in any shipment, as shown by weighing 50 packages taken at random, is less than that specified, the entire shipment may be rejected.

• TESTS

VI. SAMPLING

Number of Samples.

(16) Tests may be made on individual or composite samples as may be ordered. Each test sample should weigh at least 8 lbs.

(17) (a) *Individual Sample.*—If sampled in cars, one test sample shall be taken from each 50 barrels or fraction thereof. If sampled in bins, one sample shall be taken from each 100 barrels.

(17) (b) *Composite Samples*.—If sampled in cars, one sample shall be taken from one sack in each 40 sacks (or 1 barrel in each 10 barrels) and combined to form one test sample. If sampled in bins or warehouses, one test sample shall represent not more than 200 barrels.

Method of Sampling.

(18) Cement may be sampled at the mill by any of the following methods that may be practicable, as ordered:—

(a) From the conveyor delivering to the bin.—At least 8 lbs. of cement shall be taken from approximately each 100 barrels passing over the conveyor.

(b) From filled bins by means of proper sampling tubes.—Tubes inserted vertically may be used for sampling cement to a maximum depth of 10 feet. Tubes inserted horizontally may be used where the construction of the bin permits. Samples shall be taken from points well distributed over the face of the bin.

(c) From filled bins at points of discharge.—Sufficient cement shall be drawn from the discharge openings to obtain samples representative of the cement contained in the bin, as determined by the appearance at the discharge openings of indicators placed on the surface of the cement directly above these openings before drawing of the cement is started.

Treatment of Sample

(19) Samples preferably shall be shipped and stored in airtight containers. Samples shall be passed through a sieve having 20 meshes per linear inch in order to thoroughly mix the sample, break up lumps and remove foreign materials.

VII. CHEMICAL ANALYSIS

Loss on Ignition.

(20) *Method*.—One gr. of cement shall be heated in a weighed covered platinum crucible, of 20 to 25 c.c. capacity, as follows, using either method (a) or (b) as ordered:—

(a) The crucible shall be placed in a hole in an asbestos board, clamped horizontally so that about three-fifths of the crucible projects below, and blasted at a full red heat for 15 minutes with an inclined flame: the loss in weight shall be checked by a second blasting for 5 minutes. Care shall be taken to wipe off particles of asbestos that may adhere to the crucible when

withdrawn from the hole in the board. Greater neatness and shortening of the time of heating are secured by making a hole to fit the crucible in a circular disc of sheet platinum and placing this disc over a somewhat larger hole in an asbestos board.

(b) The crucible shall be placed in a muffle at any temperature between 900°C. and 1000°C. for 15 minutes, and the loss in weight shall be checked by a second heating for five minutes.

(21) *Permissible Variation.*—A permissible variation of 0.25 will be allowed, and all results in excess of the specified limit but within this permissible variation shall be reported as 4 %.

Insoluble Residue.

(22) *Method.*—To a 1 gr. sample of cement shall be added 10 c.c. of water and 5 c.c. of concentrated hydrochloric acid; the liquid shall be warmed until effervescence ceases. The solution shall be diluted to 50 c.c. and digested on a steam bath or hot plate until it is evident that decomposition of the cement is complete. The residue shall be filtered, washed with cold water, and the filter-paper and contents digested in about 30 c.c. of a 5 % solution of sodium carbonate, the liquid being held at a temperature just short of boiling for 15 minutes. The remaining residue shall be filtered, washed with cold water, then with a few drops of hot hydrochloric acid, 1 : 9, and finally with hot water, and then ignited at a red heat and weighed as the insoluble residue.

(23) *Permissible Variation.*—A permissible variation of 0.15 will be allowed, and all results in excess of the specified limit but within this permissible variation shall be reported as 0.85 %.

Sulphuric Anhydride.

(24) *Method.*—One gr. of the cement shall be dissolved in 5 c.c. of concentrated hydrochloric acid diluted with 5 c.c. of water, with gentle warming; when solution is complete 40 c.c. of water shall be added, the solution filtered, and the residue washed thoroughly with water. The solution shall be diluted to 150 c.c., heated to boiling and 10 c.c. of a hot 10 % solution of barium chloride shall be added slowly, drop by drop, from a pipette, and the boiling continued until the precipitate is well formed. The solution shall be digested on the steam bath until the precipitate has settled. The precipitate shall be filtered, washed, and the paper and contents placed in a weighed platinum crucible and the paper slowly charred and consumed without

flaming. The barium sulphate shall then be ignited and weighed. The weight obtained multiplied by 34.3 gives the percentage of sulphuric anhydride. The acid filtrate obtained in the determination of the insoluble residue may be used for the estimation of sulphuric anhydride instead of using a separate sample.

(25) *Permissible Variation.*—A permissible variation of 0.10 will be allowed, and all results in excess of the specified limit but within this permissible variation shall be reported as 2 %.

Magnesia.

(26) *Method.*—To 0.5 gr. of the cement in an evaporating dish shall be added 10 c.c. of water to prevent lumping, and then 10 c.c. of concentrated hydrochloric acid. The liquid shall be gently heated and agitated until attack is complete. The solution shall then be evaporated to complete dryness on a steam or water bath. To hasten dehydration, the residue may be heated to 150° C. or even 200° C. for one-half to one hour. The residue shall be treated with 10 c.c. of concentrated hydrochloric acid diluted with an equal amount of water. The dish shall be covered and the solution digested for 10 minutes on a steam bath or water bath. The diluted solution shall be filtered and the separated silica washed thoroughly with water.¹

Five c.c. of concentrated hydrochloric acid and sufficient bromine water to precipitate any manganese which may be present shall be added to the filtrate (about 250 c.c.). This shall be made alkaline with ammonium hydroxide, boiled until there is but a faint odour of ammonia, and the precipitated iron and aluminum hydroxides, after settling, shall be washed with hot water, once by decantation and slightly on the filter. Setting aside the filtrate, the precipitate shall be transferred by a jet of hot water to the precipitating vessel and dissolved in 10 c.c. of hot hydrochloric acid. The paper shall be extracted with acid, the solution and washings being added to the main solution.

The aluminum and iron shall then be re-precipitated at boiling-heat by ammonium hydroxide and bromine water in a volume of about 100 c.c., and the second precipitate shall be collected and washed on the filter used in the first instance if this is still intact. To the combined filtrates from the hydroxides of iron and aluminum, reduced in volume if need be, 1 c.c. of ammonium

¹ Since this procedure does not involve the determination of silica, a second evaporation is unnecessary.

hydroxide shall be added, the solution brought to boiling, 25 c.c. of a saturated solution of boiling ammonium oxalate added, and the boiling continued until the precipitated calcium oxalate has assumed a well-defined granular form.

The precipitate after one hour shall be filtered and washed, then with the filter shall be placed wet in a platinum crucible and the paper burned off over a small flame of a Bunsen burner; after ignition it shall be re-dissolved in hydrochloric acid and the solution diluted to 100 c.c. Ammonia shall be added in slight excess, and the liquid boiled. The lime shall then be re-precipitated by ammonium oxalate, allowed to stand until settled, filtered and washed. The combined filtrates from the calcium precipitates shall be acidified with hydrochloric acid, concentrated on the steam bath to about 150 c.c. and made slightly alkaline with ammonium hydroxide, boiled and filtered (to remove a little aluminum and iron, and perhaps calcium). When cool, 10 c.c. of saturated solution of sodium-ammonium-hydrogen phosphate shall be added, with constant stirring. When the crystalline ammonium-magnesium orthophosphate has formed, ammonia shall be added in moderate excess.

The solution shall be set aside for several hours in a cool place, filtered and washed with water containing 2.5 % of NH_3 . The precipitate shall be dissolved in a small quantity of hot hydrochloric acid, the solution diluted to about 100 c.c. of a saturated solution of sodium-ammonium-hydrogen phosphate added, and ammonia drop by drop, with constant stirring, until the precipitate is again formed as described and the ammonia is in moderate excess. The precipitate shall then be allowed to stand about two hours, filtered and washed as before. The paper and contents shall be placed in a weighed platinum crucible, the paper slowly charred, and the resulting carbon carefully burned off. The precipitate shall then be ignited to constant weight over a Meker burner, or a blast not strong enough to soften or melt the pyro-phosphate. The weight of magnesium pyrophosphate obtained multiplied by 72.5 gives the percentage of magnesia.

The precipitate so obtained always contains some calcium and usually small quantities of iron, aluminum and manganese as phosphate.

(27) *Permissible Variation.*—A permissible variation of 0.4 will be allowed, and all results in excess of the specified limit but within this permissible variation shall be reported as 5 %.

VIII. DETERMINATION OF SPECIFIC GRAVITY

Apparatus.

(28) The determination of specific gravity shall be made with a standardised Le Chatelier apparatus which conforms to the requirements illustrated in Fig. 81. This apparatus is standardised by the United States Bureau of Standards. Kerosene free from water, or benzene not lighter than 62° Baumé, shall be used in making this determination.

Method.

(29) The flask shall be filled with either of these liquids to a point on the stem between zero and 1 c.c., and 64 gr. of cement, of the same temperature as the liquid, shall be slowly introduced, taking care that the cement does not adhere to the inside of the flask above the liquid, and to free the cement from air by rolling the flask in an inclined position. After all the cement is introduced, the level of the liquid will rise to some division of the graduated neck; the difference between readings is the volume displaced by 64 gr. of the cement.

The specific gravity shall then be obtained from the formula—

$$\text{Specific gravity} = \frac{\text{Weight of cement (gr.)}}{\text{Displaced volume (c.c.)}}$$

(30) The flask, during the operation, shall be kept immersed in water in order to avoid variations in the temperature of the liquid in the flask, which shall not exceed 0.5° C. The results of repeated tests should agree within 0.01.

(31) The determination of specific gravity shall be made on the cement as received; if it falls below 3.10, a second determination shall be made after igniting the sample as described in section 20.

IX. DETERMINATION OF FINENESS

Apparatus.

(32) Wire cloth for standard sieves for cement shall be woven (not twilled) from brass, bronze, or other suitable wire, and mounted without distortion on frames not less than 1½ in. below the top of the frame. The sieve frames shall be circular, approximately 8 in. in diameter, and may be provided with a pan and cover.

(33) A standard No. 200 sieve is one having nominally an 0.0029 in. opening and 200 wires per inch standardised by the

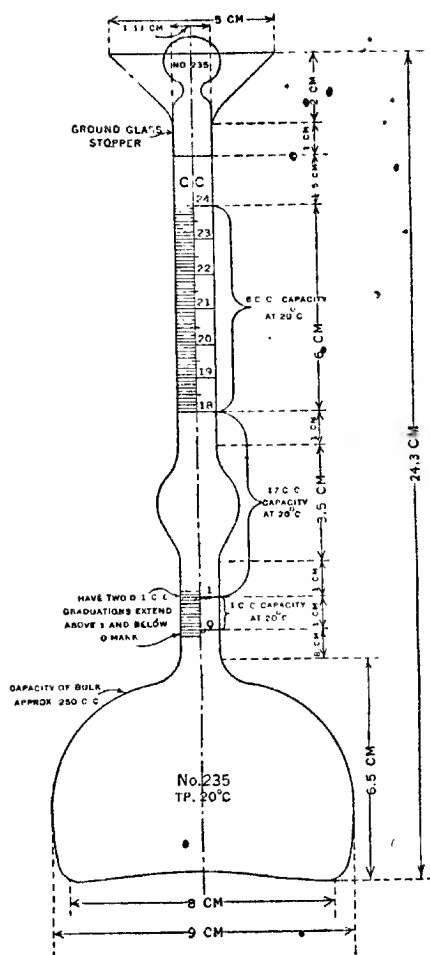


FIG. 81.—Le Chatelier's Specific Gravity Apparatus.

United States Bureau of Standards, and conforming to the following requirements—

The No. 200 sieve should have 200 wires per inch, and the number of wires in any whole inch shall not be outside the limits of 192 to 208. No opening between adjacent parallel wires shall

be more than 0.0050 in. in width. The diameter of the wire should be 0.0021 in., and the average diameter shall not be outside the limits 0.0019 in. to 0.0023 in. The value of the sieves determined by sieving tests made in conformity with the standard specification for these tests on a standardised cement which gives a residue of 25 to 20 % on the No. 200 sieve, or on other similarly graded material, shall not show a variation of more than 1.5 % above or below the standards maintained at the Bureau of Standards.

Method.

(34) The test shall be made with 50 gr. of cement. The sieve shall be thoroughly clean and dry. The cement shall be placed on the No. 200 sieve, with pan and cover attached, if desired, and shall be held in one hand in a slightly inclined position, so that the sample will be well distributed over the sieve, at the same time gently striking the side about 150 times per minute against the palm of the other hand on the upstroke. The sieve shall be turned every 25 strokes about one-sixth of a revolution in the same direction. The operation shall continue until not more than 0.05 gr. passes through in one minute of continuous sieving. The fineness shall be determined from the weight of the residue on the sieve expressed as a percentage of the weight of the original sample.

(35) Mechanical sieving devices may be used, but the cement shall not be rejected if it meets the fineness requirement when tested by the hand method described in section 34.

Permissible Variation.

(36) A permissible variation of 1 will be allowed, and all results in excess of the specified limit but within this permissible variation shall be reported as 22 %.

X. MIXING CEMENT PASTES AND MORTARS

Method.

(37) The quantity of dry material to be mixed at one time shall not exceed 1000 gr., nor be less than 500 gr. The proportions of cement, or cement and sand, shall be stated by weight in grams of the dry materials: the quantity of water shall be expressed in cubic centimetres (1 c.c. of water = 1 gr.). The dry materials shall be weighed, placed upon a non-absorbent surface, thoroughly mixed dry if sand is used, and a crater formed in

the centre, into which the proper percentage of clean water shall be poured; the material on the outer edge shall be turned into the crater by the aid of a trowel. After an interval of one-half minute for the absorption of the water the operation shall be completed by continuous, vigorous mixing, squeezing, and kneading with the hands for at least one minute.¹ During the operation of mixing, the hands should be protected by rubber gloves.

(38) The temperature of the room and the mixing-water shall be maintained as nearly as practicable at 21° C. (70° F.).

XI. NORMAL CONSISTENCY

Apparatus.

(39) The Vicat apparatus consists of a frame, bearing a movable rod weighing 300 gr., one end being 1 cm. in diameter for a distance of 6 cm., the other having a removable needle 1 mm. in diameter, 6 cm. long. The rod is reversible, and can be held in any desired position by a screw, and has midway between the ends a mark which moves a scale (graduated to millimetres) attached to the frame. The paste is held in a conical, hard-rubber ring, 7 cm. in diameter at the base, 4 cm. high, resting on a glass plate about 10 cm. square.

Method.

(40) In making the determination, 500 gr. of cement, with a measured quantity of water, shall be kneaded into a paste, as described in section 37, and quickly formed into a ball with the hands, completing the operation by tossing it six times from one hand to the other, maintained about 6 in. apart; the ball, resting in the palm of one hand, shall be pressed into the larger end of the rubber ring held in the other hand, completely filling the ring with paste; the excess at the larger end shall then be removed by a single movement of the palm of the hand; the ring shall then be placed on its larger end on a glass plate and the excess paste at the smaller end sliced off at the top of the ring by a single oblique stroke of a trowel held at a slight angle

¹ In order to secure uniformity in the results of tests for the time of setting and tensile strength, the manner of mixing above described should be carefully followed. At least one minute is necessary to obtain the desired plasticity, which is not appreciably affected by continuing the mixing for several minutes. The exact time necessary is dependent upon the personal equation of the operator. The error in mixing should be on the side of over-mixing.

with the top of the ring. During these operations care shall be taken not to compress the paste. The paste confined in the ring, resting on the plate, shall be placed under the rod, the large end of which shall be brought in contact with the surface of the paste, the scale shall be then read and the rod quickly released.

The paste shall be of normal consistency when the rod settles to a point 10 mm. below the original surface in one-half minute after being released. The apparatus shall be free from all vibrations during the test.

Trial pastes shall be made with varying percentage of water until the normal consistency is obtained. The amount of water required shall be expressed in percentage by weight of the dry cement.

(41) The consistency of standard mortar shall depend on the amount of water required to produce a paste of normal consistency from the same sample of cement. Having determined the normal consistency of the sample, the consistency of standard mortar made from the same sample shall be as indicated in the following table, the values being in percentage of the combined dry weights of the cement and standard sand.

Percentage of Water for Standard Mortars.

Percentage of water for neat cement paste of normal consistency.	Percentage of water for one cement, three standard Ottawa sand.
15	9.0
16	9.2
17	9.3
18	9.5
19	9.7
20	9.8
21	10.0
22	10.2
23	10.3
24	10.5
25	10.7
26	10.8
27	11.0
28	11.2
29	11.3
30	11.5

XII. DETERMINATION OF SOUNDNESS

Apparatus.

(42) A steam apparatus, which can be maintained at a temperature between 98° C. and 100° C., is recommended. The

capacity of this apparatus may be increased by using a rack for holding the pats in a vertical or inclined position.

Method.

(43) A pat from cement paste of normal consistency about 3 in. in diameter, $\frac{1}{2}$ in. thick at the centre, and tapering to a thin edge, shall be made on clean glass plates about 4 in. square, and stored in moist air for 24 hours. In moulding the pat, the cement paste shall first be flattened on the glass and the pat then formed by drawing the trowel from the outer edge towards the centre.

(44) The pat shall then be placed in an atmosphere of steam at a temperature between 98° C. and 100° C. upon a suitable support 1 in. above boiling water for five hours.

(45) Should the pat leave the plate, distortion may be detected best with a straight edge applied to the surface which was in contact with the plate.

XIII. DETERMINATION OF TIME OF SETTING

(46) The following are alternate methods, either of which may be used as ordered—

Vicat Apparatus.

(47) The time of setting shall be determined with the Vicat apparatus described in section 39.

(48) A paste of normal consistency shall be moulded in the hard-rubber ring, as described in section 40, and placed under the rod, the smaller end of which shall then be carefully brought in contact with the surface of the paste, and the rod quickly released. The initial set shall be said to have occurred when the needle ceases to pass a point 5 mm. above the glass plate in one-half minute after being released; and the final set, when the needle does not sink visibly into the paste. The test pieces shall be kept in moist air during the test. This may be accomplished by placing them on a rack over water contained in a pan and covered by a damp cloth, kept from contact with them by means of a wire screen, or they may be stored in a moist closet. Care shall be taken to keep the needle clean, as the collection of cement on the sides of the needle retards the penetration, while cement on the point may increase the penetration.

The time of setting is affected not only by the percentage and temperature of the water used and the amount of kneading the

paste receives, but by the temperature and humidity of the air, and its determination is therefore only approximate.

Gillmore Needles.

(49) The time of setting shall be determined by the Gillmore needles. The Gillmore needles should preferably be mounted, as shown in Fig. 82.

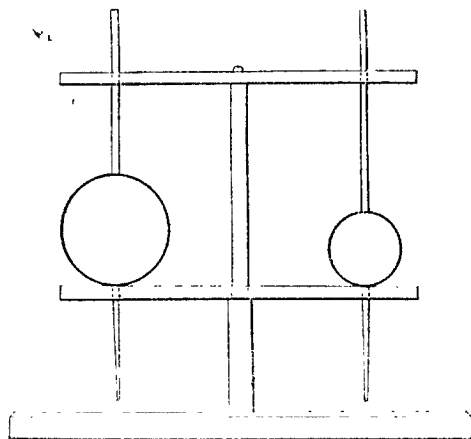


FIG. 82.—Gillmore Needles.

Gillmore Method.

(50) The time of setting shall be determined as follows:—A pat of neat cement paste about 3 in. in diameter and $\frac{1}{2}$ in. in thickness with a flat top (Fig. 83), mixed to a normal consistency,

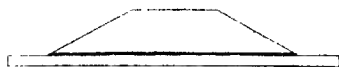


FIG. 83.—Setting-time Pat.

shall be kept in moist air at a temperature maintained as nearly as practicable at 21° C. (70° F.). The cement shall be considered to have acquired its initial set when the pat will bear, without appreciable indentation, the Gillmore needle one-twelfth in. in diameter, loaded to weigh one-fourth pound. The final set has been acquired when the pat will bear, without appreciable indentation, the Gillmore needle one twenty-fourth in. in

diameter, loaded to weigh one pound. In making the test, the needles shall be held in a vertical position, and applied lightly to the surface of the pat.

XIV. TENSION TESTS

Form of Test Piece.

(51) The form of test piece shown in Fig. 84 shall be used. The moulds shall be made of non-corroding metal and have

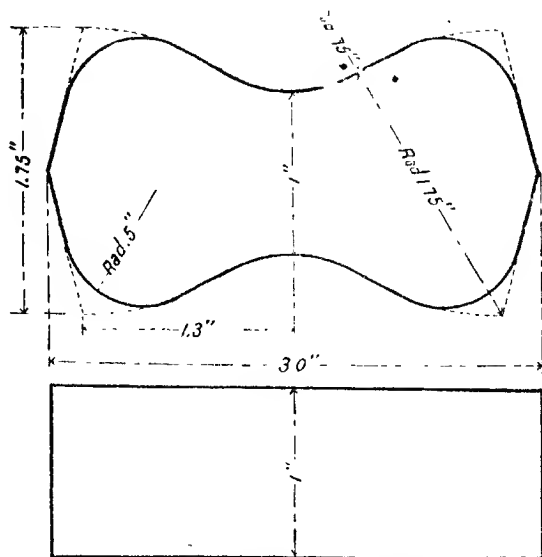


FIG. 84.—Standard Briquette. (American.)

sufficient material in the sides to prevent spreading during moulding. Gang moulds may also be used. Moulds shall be wiped with an oily cloth before using.

Standard Sand.

(52) The sand to be used shall be natural sand from Ottawa, Ill., screened to pass a No. 20 sieve and retained on a No. 30 sieve. This sand may be obtained from the Ottawa Silica Co., at a cost of 2 cents per pound f.o.b. cars, Ottawa, Ill.

(53) This sand, having passed the No. 20 sieve, shall be considered standard when not more than 5 gr. pass the No. 30 sieve after one minute continuous sieving of a 500 gr. sample.

(54) The sieves shall conform to the following specifications—

The No. 20 sieve shall have between 19.5 and 20.5 wires per whole inch of the warp wires, and between 19 and 21 wires per whole inch of the shoot wires. The diameter of the wire should be 0.0165 in., and the average diameter shall not be outside the limits of 0.0160 and 0.0170 in.

The No. 30 sieve shall have between 29.5 and 30.5 wires per whole inch of the warp wires, and between 28.5 and 31.5 wires per whole inch of the shoot wires. The diameter of the wire should be 0.0110 in., and the average diameter shall not be outside the limits 0.0105 to 0.0115 in.

Moulding.

(55) Immediately after mixing the standard mortar shall be placed in the moulds, pressed in firmly with the thumbs, and smoothed off with a trowel without ramming. Additional mortar shall be heaped above the mould and smoothed off with a trowel; the trowel shall be drawn over the mould in such a manner as to exert a moderate pressure on the material. The mould shall then be turned over and the operation of heaping, thumbing, and smoothing off repeated.

Testing.

(56) Tests shall be made with any standard machine. The briquettes shall be tested as soon as they are removed from the water. The bearing surfaces of the clips and briquettes shall be free from grains of sand or dirt. The briquettes shall be carefully centred and the load applied continuously at the rate of 600 pounds per minute.

(57) Testing machines should be frequently calibrated in order to determine their accuracy.

Faulty Briquettes.

(58) Briquettes that are manifestly faulty, or which give strengths differing more than 15 % from the average value of all test pieces made from the sample and broken at the same period shall not be considered in determining the tensile strength.

XV. STORAGE OF TEST PIECES

Apparatus.

(59) The moist closet may consist of a soapstone or concrete box, or a wooden box lined with metal. If a wooden box is used, the interior should be covered with felt or broad wicking kept wet. The bottom of the moist closet should be covered with water. The interior of the closet should be provided with non-absorbent shelves on which to place the test pieces, the shelves being so arranged that they may be withdrawn readily.

Methods.

(60) Unless otherwise specified, all test pieces, immediately after moulding, shall be placed in the moist closet for from 20 to 24 hours.

(61) The briquettes shall be kept in moulds on glass plates in the moist closet for at least 20 hours. After 24 hours in moist air the briquettes shall be immersed in clean water in storage tanks of non-corroding material.

(62) The air and water shall be maintained as nearly as practicable at a temperature of 21° C. (70° F.).

FRENCH GOVERNMENT SPECIFICATION

MINISTERIAL DECREE

CONCERNING

THE SUPPLY OF CEMENTS AND HYDRAULIC LIME

Issued by the Ministry of Public Works, June 2, 1902.

Modified, November 29, 1904, November 9, 1909,
and December 24, 1910.

General Regulations.—The entire supply of cement and lime concerned with the execution of the works dependent of the Administration of Public Works, whether in case of contracts with supply without use or those with both supply and employ, is to be subject to the following regulations, in all respects applicable to them.

Mode of Delivery.—The cement and lime, when supplied in powder, are to be delivered in sacks or barrels.

The sacks are to contain a net weight of 25 or 50 kilos; they are to be stitched inside and closed by means of a lead seal with the manufacturer's trade mark, in a manner approved by the Administration.

The barrels are to have on one of their ends the trade mark, and on the other the net weight of cement or lime which they contain.

The sacks or barrels shall be in perfect condition at the time of delivery. All cement and lime which has been affected by damp will be rejected.

On the arrival of each delivery, the bills of lading or freight notes will be communicated to the engineer.

Storage.—The sacks or barrels of cement or lime will be kept in very dry storehouses, closed and covered in. They will be placed there in distinct heaps, corresponding to each delivery.

The contractor will have the care of and responsibility for the cement and lime in the storehouse until the moment of use.

All sacks or barrels of cement or of lime which may be injured, or the coverings of which are not in good condition at the time of delivery for use, will be rejected.

Tests.—No cement or lime may be used without having been submitted to the tests prescribed by the specification specially made out by the authorities, and accepted provisionally.

The engineer will have the right to carry out repeatedly, during the whole time of storage of the lime and cement, accepted provisionally, the tests required by the particular specifications of the authorities, and to reject the lots which do not satisfy these, at the moment when they are delivered for use, or at that of the final reception, on the conditions required for these tests.

If the tests give unfavourable results, the contractor may require them to be made again in the laboratory of the École des Ponts et Chaussées.

Selection of Samples.—The samples to be submitted to the tests are to be taken at different depths and positions, from several sacks, barrels or heaps designated by the engineer. The cement or lime taken from different places shall not be mixed together.

Quality.—The cement or lime must be of uniform composition and quality. It shall contain no unburnt or foreign matter.

Fineness of the Grinding.—The tests will be carried out on a sample of 100 gr. The sifting will be effected by means of

a sieve of 324, 900 or 4,900 meshes per square cm., the wires of these three sieves are to have the respective thicknesses of twenty, fifteen or five-hundredths of a mm.

Apparent Density.—The apparent density will be ascertained by pouring the cement or lime gently, without letting it heap up, into a metal measure of cylindrical shape, with a capacity of 1 litre and a height of 10 cm.

The cement or lime contained in the measure will be weighed. For the apparent density, the average of the weights ascertained in three successive operations will be taken.

In case of doubt, the measure will be filled again by means of a funnel, with a sieve bottom in perforated metal plate, with holes of 2 mm. each; this funnel is so placed that its narrow end is 5 cm. above the measure. The cement or lime is poured in gradually without any shock or agitation. When the measure is full, the superfluous matter is removed by passing over its upper edge a sheet of metal held vertically.

Duration of Setting.—The cement or lime is mixed with fresh water into a stiff paste, and made into the form of a pat of a thickness of 4 cm. approximately, which must be then plunged either into fresh or salt water, according to the instructions given in the specifications of the authorities. The cement or lime, the mixing water, and the immersion bath are to be at the temperature of at least 15° C., in the case of fixing the maximum rapidity of setting, and of at most 15° C. in the case of fixing the minimum.

The setting is considered to begin from the moment when the standard needle, with a section of one sq. mm. and a weight of 300 gr., can no longer pass through the whole cake.

The setting is considered to end at the moment when the surface of the pat can support the same needle without its penetrating to any appreciable extent, such as 0.1 mm.

In case of dispute, the term stiff paste shall be determined as follows:—The paste shall be gauged at the rate of 5 minutes per kilo and filled into a mould 4 cm. deep. This paste shall be pierced to within 6 mm. of the bottom of the mould by a consistency plunger of 1 cm. diameter and weighing 300 gr.

Tensile Strength.—The tests of tensile strength may be made on the stiff paste of cement or pure lime, and on the plastic mortar of cement or lime steeped in fresh water. They will be carried out by means of test pieces in figures of 8, with a middle section of 5 square mm.

The moulds used in making the test pieces are filled in one operation, being first shaken to expel air-bubbles. The paste or mortar is then compressed with a trowel, but not beaten down; then, with the blade of the trowel, the surplus matter is removed from the edges of the mould, and the surface is smoothed.

Each test entails the breaking of six samples. The resistance to traction is estimated at the average of the four highest results.

The mortar is to be made up in weight at the rate of one part of cement or lime to three of dry sand. The sand is to be composed of equal parts of grains of three sizes separated by the four sieves of metal plate perforated by holes, $\frac{1}{2}$, 1, $1\frac{1}{2}$, and 2 mm. diameter.

The samples, after having been kept in a damp atmosphere, sheltered from draughts and from the sun during a time the duration of which has been fixed by the particular specification of the authorities, are to be taken out of the moulds, and immersed in fresh water, according to the directions of the specification. In every case the water is to be removed once a week.

In case of doubt, the firm paste of cement or of pure lime is regarded as being that which is defined as for setting time, and the plastic mortar of cement or lime as a mortar made by means of sand from the beach of Leucate, supplied by the Administration, and moistened by a quantity of water equal for a kilo of dry material to 55 gr. plus 1 P., P. being the weight of water necessary to transform one kilo of cement or of lime into a firm paste.

The tests of distortion under the influence of cold will be made with pats of cement or lime worked into a firm paste with fresh water. The pats are about 10 cm. in diameter and 2 cm. thick, and are thinned at the edges and placed on plates of glass. The pats will be steeped under conditions fixed by the particular specification of the authorities, and will be kept in the water until the cement or lime has been definitely accepted.

None of the pats must have the least sign of blowing or buckling. The edges of the pats must adhere firmly to the glass, and must not rise at any place.

The tests of distortion under the influence of heat will be made on cylindrical test pieces of a diameter and height of 30 mm. moulded in a brass tube half a mm. in thickness, split vertically and having a needle soldered on each side of the opening, 150 mm. in length.

During the twenty-four hours following gassing, the test pieces are to be immersed in water, which is to be raised by degrees to a temperature fixed by the specification and then chilled to the initial temperature. The increase of distance between the points of the needles must never exceed the distance laid down in the specifications.

None of the pats or test pieces must show the least trace of blowing or distortion, or any cracks, or other defects. The edges of the pats must remain adhering to the glass, and must not rise in any place.

The water in which the test pieces and pats are stored must be kept at a temperature between 12° C. and 18° C.

The cement and lime rejected are to be taken away from the warehouses by and at cost of the contractor within ten days, dating from the official notification of rejection.

SPECIFICATION, TYPE NO. 1

FOR THE SUPPLY OF PORTLAND CEMENT INTENDED FOR WORKS LYING OPEN TO THE SEA

Definition of the Product.—The Portland cement is to be produced by grinding an intimate mixture of carbonate of lime, silica, alumina and iron, and burning to incipient fusion.

Origin and Inspection at Factory.—The cement is to be supplied directly and exclusively from (the name of works to be specified).

The Administration reserves the right to exercise control at the works, both with respect to the manufacture, the preservation and delivery of the cement supplied in fulfilment of the present contract.

Special inspectors may be appointed permanently for this purpose.

Mode of Delivery.—The cement shall be delivered (in sacks or barrels).

Chemical Composition.—The cement must not contain more than 1.5 % of sulphuric acid, or more than 2 % of magnesia, or 8 % of alumina, or more than traces of sulphides.

The hydraulic coefficient—i. e. the proportion between the weight of the combined silica and alumina on the one side, and the weight of lime and magnesia on the other side—is to be at least 0.47 for a content of alumina of 8 %, with a decrease of 0.02 for each 1 % of alumina below 8.

Fineness of Grinding.—The cement should leave at most 10 % of its weight on the sieve of 900 meshes per sq. cm.

Apparent Density.—The weight per litre of cement is to be 1,200 gr. at least.

Setting Time.—The cement immersed in fresh water must not begin to set until twenty minutes have passed.

The setting must be completely finished in a period of not less than three or more than twelve hours.

Tensile Strength of Neat Cement.—The briquettes of neat cement, when immersed in sea water, at the end of twenty-four hours, must show a resistance or tensile strength per sq. cm. of at least—

25 kilos at the end of 7 days.

35 kilos at the end of 28 days.¹

The resistance must be increased by at least three kilos from the seventh to the twenty-eighth day.

Tensile Strength of the Cement Mortar.—Briquettes of mortar, when immersed in sea water, at the end of twenty-four hours, must show tensile strength per sq. cm. of at least—

8 kilos at the end of a week.

15 kilos at the end of 28 days.²

The resistance must be increased by at least 2 kilos from the seventh to the twenty-eighth day.

Distortion under Cold and Heat.—The pats and test pieces are to be kept in a damp atmosphere for twenty-four hours; the pats are then to be immersed in sea water. The temperature of the test by distortion under the influence of heat shall be 100° C.; it is to be kept up for three hours. The increase of the distance between the points of the needles must not exceed 5 mm.

SPECIFICATION, TYPE NO. 3

FOR THE SUPPLY OF PORTLAND CEMENT INTENDED FOR WORKS
NOT LYING OPEN TO THE SEA

Definition of the Product.—The Portland cement is to be produced by grinding an intimate mixture of carbonate of lime, silica, alumina and iron, and burning to incipient fusion.

¹ The figures given are to be regarded as a minimum. The engineers can increase them after being satisfied that the works can supply his requirements.

² Same observation as Art. 8. The minimum resistance required was reduced from 12 to 11 kilos by the treatise of November 29, 1904. (See further on.)

Supply and Control at the Works.—The cement is to be supplied directly and exclusively by (as specified).

The Administration reserves the right to keep a control at the works, both with respect to the manufacture, the preservation and the delivery of the cement supplied in fulfilment of the present contract.

Special inspectors may be appointed permanently for this purpose.

Mode of Delivery.—The cement is to be delivered (in sacks or in barrels).

Chemical Composition.—The cement must not contain more than 3 % of sulphuric acid, or more than 5 % of magnesia, or more than 10 % of alumina, or more than traces of sulphides.

Fineness of Grinding.—The cement must leave at most 30 % of its weight on the sieve of 4,900 meshes per sq. cm., and 10 % on the sieve of 900 meshes.

Apparent Density.—The weight of the litre of cement must be at least 1,100 gr.

Setting Time.—The cement immersed in fresh water must not begin to set until twenty minutes have elapsed.

The setting must be completely finished in a period of not less than two hours or more than twelve hours.

Tensile Strength of Neat Cement.—The briquettes of neat cement immersed in fresh water at the end of twenty-four hours must show a tensile strength per sq. cm. of at least—

25 kilos at the end of 7 days.

35 kilos at the end of 28 days.¹

The resistance must be increased by at least 3 kilos from the seventh to the twenty-eighth day.

Tensile Strength of Cement Mortar.—The test pieces of mortar, immersed in fresh water at the end of twenty-four hours, must show a tensile strength per sq. cm. of at least—

8 kilos at the end of 7 days.

15 kilos at the end of 28 days.¹

The resistance must be increased by at least 2 kilos from the seventh day to the twenty-eighth day.

Distortion under the Influence of Heat.—The test samples will be kept in a damp atmosphere during twenty-four hours. The

¹ The figures given are the minimum. The engineers can increase them after being assured that the works are in a position to obtain what they require.

testing temperature will be 100° C., and will be kept up for three hours. The increase of the distance between the points of the needles must not exceed 10 mm.

ITALIAN SPECIFICATION ISSUED BY THE MINISTRY OF
PUBLIC WORKS

RULES AND CONDITIONS
FOR THE TESTING AND RECEPTION OF
HYDRAULIC CEMENTS

AND
STANDARD REGULATIONS

FOR THE EXECUTION OF WORKS IN
REINFORCED CONCRETE

Approved of by Ministerial Decree of January 10th, 1912.

STANDARD METHODS FOR TESTING
HYDRAULIC CEMENTS

PART I

GENERAL REGULATIONS

I. FINENESS OF GRINDING

THE fineness of the grinding will be determined by means of square-meshed sieves, with 900 and 4,900 meshes per sq. cm., made of wires of a respective diameter of 0.15 and 0.05 mm.

The tests are to be made on two samples of 50 gr. each, and the percentage is to be calculated from the two results obtained.

Hand sifting will be considered completed when, after 25 revolutions of the arm, the material which has passed through the sieve is not more than 0.10 gr.

The result of a sifting will be ascertained by calculating the residue which has not passed through the sieve.

II. SPECIFIC GRAVITY

The determination of the specific gravity may be made with any of the methods already known, provided that the apparatus used enables us to ascertain exactly the first and second decimal figure, with an approximation of two units.

It is necessary to make certain, before testing, that the material has been previously dried and thoroughly pulverised so that it will pass through a sieve of 900 meshes.

During the operations for the determination of the density, the temperature of the apparatus, of the material and the liquid must be about 15° C.

III. APPARENT DENSITY

The apparent density will be given by the weight of a cylindrical measure, with circular section, of the capacity of 1 litre and of a height of 10 cm., filled by means of a sifting funnel.

The apparatus consists of a vertical funnel, the section of which horizontally at the base is a circle 20 mm. in diameter, and at 150 mm. above the base is a circle of a diameter of 150 mm. At this height a perforated plate is put in, with about 1,050 holes of 2 mm. diameter for each sq. cm.

The funnel is prolonged by means of a cylindrical tube of 20 mm. diameter and 100 mm. length, and is sustained on a tripod.

When the measure is placed under the funnel, at a distance of 50 mm. from the lower end of the cylindrical tube, the cement is poured on the perforated plate in amounts of about 300 gr. at a time, and this is stirred about by a sort of wooden shovel 40 mm. wide to facilitate the passage of the cement through. The filling of the measure is stopped when the base of the cone, which is gradually raised above the same, reaches the upper end of the measure. The excess of material is removed by passing over the upper edge of the measure a level plate of metal, keeping it in a vertical plane.

During the whole time of these operations, care must be taken not to shake the measure of the apparatus.

The weight per litre will be ascertained from the average obtained with the results of three consecutive operations.

IV. STANDARD PASTE

On a slab of marble there is spread out in the shape of a wreath 1 kilo of cement, into the middle of which there is

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During the whole time of these operations, care must be taken not to shake the measure of the apparatus.

The weight per litre will be ascertained from the average obtained with the results of three consecutive operations.

IV. STANDARD PASTE

On a slab of marble there is spread out in the shape of a wreath 1 kilo of cement, into the middle of which there is

poured at one stroke the quantity of fresh water considered necessary to obtain a paste of the consistency indicated below; then the whole is stirred together vigorously with a ladle for three minutes, counting from the beginning of the operation of mixing.

With a portion of the paste thus obtained, an ebonite or metal box is filled at once, the diameter of the said box being 0.08 m. at the base, 0.09 m. diameter at the top, and 0.04 m. deep; then the surface is smoothed with the ladle or trowel, whilst all shaking or compression should be carefully avoided.

Bring to the surface of the paste and let down carefully and without it acquiring any velocity, a cylindrical needle 0.01 m. in diameter and of the weight of 300 gr., of very smooth metal and sharp, the end terminating in a clean section, at right angles to the axis of the cylinder. This needle, which is termed "consistency needle," must be supported by a suitable stand, so made that it should be possible to determine exactly the depth of the paste penetrated.

The consistency of the paste must be such that the needle stops 6 mm. from the bottom of the mould. If this result is not obtained the operation must be repeated, the paste being re-made with a greater or lesser quantity of water, as the case may be. The paste satisfying the above conditions will be now termed standard paste.

The temperature of the atmosphere and the cement and water to be used in carrying out these operations must be not less than 15° C. or more than 20° C.

V. STANDARD SAND

The standard sand is that of which the grains pass through a metal sieve with circular holes of a diameter of 1.5 mm. and remain on another sieve, also of metal, with circular holes of a diameter of 1 mm.

Standard sand serves to make the mortar for testing hydraulic cement.

For control tests, in case of doubt, and for the furtherance of general interests, standard sand coming from Ticino will be adopted, in accordance with the decision arrived at by the Italian Association for the Examination of Building Materials at the Congress of Pisa, in the month of April, 1905.

VI. STANDARD MORTAR

Standard mortar is to be mixed in the proportion of one part of cement to three parts of standard sand, and is to be moistened with fresh water, after having been well mixed together in a dry state.

Cement, water, sand and the surrounding atmosphere must be at a temperature of between 15° and 20° C.

The mortar is to be made by means of a mixer with movable tray and compression mould, the tray revolving at the rate of 20 revolutions in two minutes and a half, *i. e.* 8 revolutions per minute.

The quantity of water required to make the mortar will be measured in such a way that it will begin to appear between the interstices of the mould during the manufacture by machinery of the briquettes, not before the 90th nor after the 100th stroke of the mallet has been given.

The quantity of water required for standard mortar will be determined by successive experiments, beginning by making the mortar by adding water in the proportion of 8 % of the weight of the mixture, and varying this by degrees until the result mentioned above is attained.

VII. SETTING TESTS

Setting tests will be carried out on the standard paste as defined in the chapter relating to the same.

Standard paste, placed in the same mould as was used for its determination, is to be kept in a damp place, sheltered from draughts and the sun's rays during the whole of the testing period, and at a mean temperature of 15° C.

The test will consist in the determination of the initial and of the final setting, using for this purpose a metal needle (termed "standard needle") which is cylindrical, smooth, polished and dry, terminating in a clean section, at right angles to the axis, of 1 sq. mm. (diameter 1.13 mm.), and weighing 300 gr.

The time of the initial setting will be considered the moment when the said needle can no longer penetrate to the bottom of the mould.

The final setting will be the moment when the needle will be supported by the paste without being able to penetrate into it to any appreciable extent (1 mm.).

The corresponding periods of time will be calculated from the moment when the paste is made.

VIII. TESTS FOR TENSILE STRENGTH

Standard mortar corresponding to 200 gr. of dry substance (mixture) is placed in the standard mould, of a minimum section of 5 sq. cm. It is then compressed within three minutes by means of 120 strokes of a mallet of the weight of 2 kilos, falling from a height of 0.25 m., and developing in this way the work of 0.35 kilos for each gr. of compressed matter.

When the hammering is concluded, the excess of mortar is carefully removed from the mould, and the surface is smoothed with the trowel, the test samples are then taken out by hand very carefully, or else mechanically removed by the aid of an automatic unmoulding machine, and are kept for twenty-four consecutive hours in a damp atmosphere at a temperature of between 15° and 20° C., and sheltered from draughts and the action of the sun.

When this period of time is over, the test samples will be immersed in fresh water.

The water is to be renewed every seven days, and kept at a constant temperature of 15° to 20° C. It must have a volume of at least four times that of the immersed briquette.

The apparatus for breaking the briquettes must be arranged and regulated so that the load is applied regularly and continuously and increases at the rate of 5 kilos per second.

The form of the jaws and the mode of making the attachment must be in accordance with the type specified.

The breaking of the briquettes will be effected as soon as they are taken out of the water, after periods of 7, 28, 84, 180, 360, etc., days, counting from the moment of the preparation of the mortar.

Each experiment will require the breaking of six briquettes, and the definite tensile strength will be taken as being the average of the four briquettes which gave the highest results.

Tensile strength tests can also be carried out on neat cement, using the standard paste therefor. This is placed in the moulds in sufficient quantity to fill each at one time, compressing it with the finger so as not to allow fissures to be formed. It is then struck with slight strokes with the trowel over and sideways so that the cement be uniform and contain no air-bubbles. Then,

with the blade of the trowel the surplus matter is removed from the mould without using too much pressure, and the surface is nicely smoothed.

The briquettes thus made are kept in their moulds for twenty-four hours, in a damp atmosphere, free from draughts and the rays of the sun, in a temperature between 15° and 20° C.

After this length of time has elapsed, the briquettes are taken out and treated like those of standard mortar.

IX. COMPRESSION STRENGTH TESTS

Standard mortar prepared as indicated in the corresponding chapter will be placed in a cubical mould of 50 sq. cm. section and in the quantity corresponding to 450 gr. of dry mixture.

The compression of the mortar is thereupon carried out by means of 160 strokes from a mallet of the weight of 3 kilos, falling from a height of 0.50 m., and consequently doing a work of compression of 0.30 kilos for each gr. of matter compressed.

With regard to storage, consecutive preservation of the cubes, periods of testing and mode of calculating the strength, the same rules are to be observed as in the heretofore mentioned paragraph relating to tensile strength tests, with the exception of the use of the automatic un moulding machine.

Tests must be made immediately after the cubes have been taken out of the bath, always bearing in mind that the force of compression must be exercised normally on two of the opposite surfaces which have been in contact with the lateral divisions of the mould, the latter being as much parallel as is permitted by the degree of accuracy of the mould itself, and the same are smoother than the upper and lower surfaces.

X. BENDING STRENGTH TESTS

Bending strength tests are to be carried out on bars of a square section of 2 cm. side length, and 12 cm. longitudinally. These bars are to be made in suitable moulds, but in case there are no proper machines to make them, they can be beaten out by hand with a piece of iron 35 cm. long (including handle), of a weight of 250 gr., with a beating surface of 25 sq. cm.

The bar to be tested shall be placed with one of the side faces which have been in contact with the mould over two knife-edges slightly rounded off, and 10 cm. distant from each other.

The weight and strain are to be applied in the middle, making use simply of a knife-edge slightly rounded off.

The breaking apparatus is to be such that the strain exercised on the bar may be increased continuously in the proportion of 1 kilo per second.

The coefficient of strength will be determined in the manner and after the periods of time laid down for the tensile and compression strength tests.

XI. COLD TEST FOR CONSTANCY OF VOLUME

The cold tests are to be carried out on the standard paste.

The same is to be spread out on glass plates, forming pats of a diameter of 0.10 to 0.15 m., and with a thickness towards the middle of 1.5 to 2 cm., taking care that the said thickness is reduced towards the perimeter, where it should be brought down to a few mm. (say about 5 mm.).

The pats are to be immersed in fresh water twenty-four hours after they are made, being kept during that period of time in a damp atmosphere, sheltered from draughts and sun rays, and at a temperature between 15° and 20° C.

After the periods indicated hereabove for tensile and compression strength tests, the pats will be taken out of the water, and the state of preservation will be observed, in order to ascertain if they show any change of shape or any radial cracks extending towards the perimeter.

XII. HOT TEST FOR CONSTANCY OF VOLUME

For the hot tests, cylindrical test pieces are used, of a diameter of 3 cm. and a height of 3 cm., made in metal moulds of the thickness of $\frac{1}{2}$ mm., split vertically, and having a needle 15 cm. long soldered on each side of the opening.

The moulds are to be filled with standard paste, and kept in a damp atmosphere, sheltered from draughts and sun rays, and at a temperature between 15° and 20° C.

After twenty-four hours, and in any case not before setting is completed, the test samples are to be immersed in fresh water at a temperature of about 16° C. Within twenty-four hours from the moment of immersion, the temperature of the water is to be raised gradually up to 100° C., in a period of time varying between a quarter of an hour and half an hour. The same temperature

is to be maintained for six consecutive hours, and the water is then to be cooled for the final measurement.

The increase in the distance between the points of the needle gives the measurement of the expansion which has taken place in the cement.

Alternative Hot Test.—Spherical test pieces may be used, their diameter ranging from 4 to 5 cm. Such test pieces are made by mixing the material with a quantity of water, 1 % less than that required to obtain the standard paste, and they are shaped from the paste itself, being rolled with the palms of the hand into spheres of 4 to 5 cm. diameter.

The spheres are kept for twenty-four hours in a damp atmosphere, sheltered from draughts and sun rays, and at a temperature of 15° to 20° C.

After the twenty-four hours have elapsed, and in any case not before the setting is completed, the spheres are placed in fresh water, in accordance with the rules indicated above for cylindrical test samples.

When the spheres are taken out of the water, they will be examined to ascertain whether they show signs of disintegration or cracking, or whether a friable material which separates when struck has resulted therefrom.

XIII. SUPPLEMENTARY TESTS

As final investigations into the properties of hydraulic cements, or to satisfy special inquiries in view of particular applications, tests can be carried out or required, which may be regarded as supplementary, because in some cases these are of secondary importance, while in other cases they may be very important indeed.

For some such tests, we cannot say that there is at all a uniformity of agreement or any unanimity as to the mode of carrying them out; therefore it seems to be sufficient to enumerate them without entering into any descriptive particulars.

Other tests (as, for instance, chemical analysis), cannot give rise to any doubt as to how they should be made, so that for these it will be enough to indicate them, without adding any special description.

These tests are—

(a) Examination of the chemical composition of the cement with special reference to sulphate of lime and magnesia.

- (b) Test of homogeneity.
- (c) Test of porosity.
- (d) Test of permeability.
- (e) Test of adherence.
- (f) Test of resistance to decomposition in sea water.
- (g) Test of resistance to cutting force.

PART II

STANDARD TESTS FOR THE ACCEPTANCE OF HYDRAULIC CEMENT MATERIALS

Hydraulic cement materials in use are divided into the following categories or groups—

Quick-setting cements.

Slow-setting Portland cements.

The same should not contain sulphates in such proportions as would exceed 1·2 % of sulphuric anhydride and of magnesia in proportion exceeding 3 %.

The physical tests for the acceptance of any of the above categories will be as follows—

Quick-setting Cements

Fineness of grinding, density, as stated in Sections I, II, III.

Standard Paste as stated in Section IV. However, the quantity of cement shall not be more than 500 gr. and the time for mixing shall be reduced to one minute.

Standard mortar as stated in Section VI. The quantity of mixture shall not be more than 500 gr. and the time for mixing shall be reduced to one minute. The mortar shall be hand-made in an iron bowl with the help of an iron scoop.

Setting tests, as stated in Section VII.

Tensile and compression strength tests as stated in Sections VIII and IX. The preparation of the test pieces shall be made by hand and shall be completed before the commencement of the setting. The periods of the tests shall be graduated as follows: after 15, 60 minutes, 24 hours, 3, 7, 28, etc., days, for neat cement, and after 1, 7, 28, etc., days for mortar.

Hot and cold tests for constancy of volume, as stated in Sections X and XI. For the heat tests, however, the temperature shall be limited to 50° C.

Slow-setting Portland Cements

For this class of hydraulic cement materials there shall be carried out the tests mentioned in the general rule concerning the standard methods for testing hydraulic cement materials according to the instructions given at the respective chapters, without any alteration whatever.

TECHNICAL SPECIFICATIONS

to which hydraulic cement materials used in the works under the control of the Ministry of Public Works shall have to comply.

I. GENERAL SPECIFICATIONS

The hydraulic cement materials, lime and cements, to be used in connection with works under the control of the Ministry of Public Works, have to be supplied in sealed bags, sewed internally with the name of the firm and the mark of the establishment they originate from, and have to be accompanied by a certificate from the manufacturer in which there shall be stated the date of manufacture of each consignment, and the results of the tests carried out in the laboratory of the manufacturing concern.

The contractors for the works are under the obligation of notifying any change of the works or the name of the establishment or establishments from which they intend to derive the hydraulic cement materials, and to produce, upon the request of the Administration, samples of the products.

At any time, either at the presentation of the said samples, or at the delivery of the supply, or during the building operations, the contractors shall give all necessary assistance for the carrying out of any tests made on the lime or cements supplied or to be supplied, being responsible for all the expenses arising in connection with the taking the samples and sending them to the testing institutes which shall be stated by the Administration, and paying the respective charges.

All tests carried out on the lime and cements, either in the laboratories of the manufacturing firm or in those stated by the Administration, shall be made according to the standard methods, as adopted by the Perugia Congress of the Italian Association for studies on building materials held in May 1906 (see Schedule A).

Wherever there are stated strength limits after a period of seven and twenty-eight days, it is always understood that the

final acceptance of the lots shall depend upon the tests in regard to the second of the two periods.

II. SPECIAL STIPULATIONS TO BE PLACED IN STANDARD TESTS

Quick-setting Cements

(a) *Fineness of Grinding*.—Should not leave a residue, more than 20 % on the sieve with 900 meshes per sq. cm.

(b) *Absolute Density*.—Shall be more than 2.80.

(c) *Setting*.—The setting of neat cement paste shall not commence before 1 minute, and the final set shall not be more than 30 minutes.

(d) *Strength*.—The test pieces made of neat cement paste of standard consistency shall bear a tensile strain of not less than 16 kilos per sq. cm. and a compression strain of not less than 160 kilos per sq. cm., after seven days under water, as from the time of the making of the paste.

Slow-setting Portland Cements

(a) *Fineness of Grinding*.—The residue left on the sieve of 900 meshes per sq. cm. shall not be more than 2 % and that on the 4,900-mesh sieve shall not be more than 20 %.

(b) *Hot and Cold Test for Constancy of Volume*.—For hot test there shall be used solely spherical cement test samples of 4 to 5 cm. in diameter.

(c) Neither the pats of cement for the cold test nor the spherical cement test pieces for the hot test should present any cracks after the tests.

(d) *Setting*.—The setting of standard paste should not commence before one hour nor finish before five hours, or after twelve hours, counting from the moment of the mixing.

(e) *Tensile Strength*.—Test pieces of standard mortar, intended for the tensile strength tests after twenty-eight days, shall not break at less than 20 kilos per sq. cm.

(f) *Compression Strength*.—The standard mortar test piece shall not break at less than 220 kilos per sq. cm. after twenty-eight days.

(g) For Portland cement which shall have already obtained provisional (preliminary) approval, isolated lots can be accepted when the breaking-strength of standard mortars after seven days shall have attained at least 16 kilos per sq. cm. for tensile strength and 180 for compression strength.

III. SUPPLEMENTARY TESTS

In such cases as may be found necessary, there may be imposed for any particular material, in addition to the tests mentioned hereabove, other tests which may be regarded as complementary, if only they are contemplated in Chapter XIII of the general prescriptions concerning the standard testing methods for hydraulic cement materials (Schedule A).

In such cases there shall be stated in the respective chapters of the coefficients and the results to be reached in the aforesaid supplementary tests.

The said materials shall not contain sulphate in proportions exceeding 1.20 % of sulphuric anhydride, nor magnesia in a proportion exceeding 3 %.

RUSSIAN SPECIFICATION OF PORTLAND CEMENT

I. DEFINITION OF PORTLAND CEMENT

The proportion by weight of oxide of calcium (CaO) to the total amount of the weight of silica (SiO_2), alumina (Al_2O_3) and of oxide of iron (Fe_2O_3) in Portland cement must not be less than 1.7 and not more than 2.2. The amount of sulphuric anhydride and magnesia in prepared Portland cement (viz. after adding foreign materials to the burnt product, see note 1) must be: the first one not more than $1\frac{3}{4}$ %, and the second not more than 3 %.

Note 1.—In order to regulate the setting, etc., of Portland cement, it is permissible to add to the burnt and pulverised cement foreign materials not exceeding 2 %.

Note 2.—The management of cement factories are entitled to appoint to the works persons authorised by the management for the purpose of supervising the preparation of cement from its proper components, and also for the purpose of making on the works part of or all the tests relating to the quality of the finished products as described by these regulations.

Should there be any doubt as to the components of the product, or when specially instructed by the proper department of the Ministry of Roads and Communications, the person appointed shall test the components by chemical analysis.

II. GENERAL INSTRUCTIONS AS TO TESTING THE QUALITIES OF PORTLAND CEMENT

(a) The testing of the quality of Portland cement as indicated in paragraphs 3 to 7, must be made in every respect according to the present technical stipulations.

(b) In order to test consignments of over 3000 casks, it is divided into lots of 3000 casks. Out of each lot 0.3 % of the number of casks is selected, and out of each cask selected 15 lbs. of cement is taken. If the supply is less than 3000 casks, the total is divided into lots of 1000 casks; $\frac{1}{3}$ % is selected from each lot, and 15 lbs. of cement taken out of each cask. Should the whole supply be less than 1000 casks, the whole supply is taken as one lot and the number of samples for testing must not be less than 3.

If the supply is less than 500 casks, the supply is accepted in a simplified way: viz. test is made as to the constancy of volume, the specific weight is determined and the results of former tests are taken into consideration.

All tests of the cement are to be made with the mixture of the samples taken out of each lot, but the constancy of volume test is to be made on each sample.

(c) The mortar for all tests and examinations is prepared with fresh or distilled water.

Note.—When testing cement for marine purposes, the mortar for all tests, except for the setting-time test, must be made with sea water.

(d) All the tests should be carried out in a room at a uniform temperature of 15° to 18° C., using the cement as well as sand and water brought up to the same temperature as that of the room. In cases where this rule as regards temperature cannot be fulfilled, it is necessary to mention the fact in the report, giving the temperature at the time of the tests.

(e) In preparing the briquettes for the tensile tests (paragraph 7), not more than six briquettes shall be gauged at one time; in any case, the preparation of briquettes must be complete before the commencement of the setting.

(f) Every gauging, either with sand or for the purpose of obtaining a paste from neat Portland cement, must last for a definite time, i. e. five minutes, reckoned from the time of the addition of the water. The mixing of cement paste, as well as the preparation of the briquettes for tensile strength tests

(paragraph 7), should be made as far as possible by the same person using the same instruments.

(g) All the test pieces, during the time of setting and previous to immersing in water, must be kept in a moist atmosphere.

In preparing the above briquettes and test pieces the gauging must be carried out upon a non-porous, smooth surface, of marble, glass or metal.

III. SPECIFIC GRAVITY OF PORTLAND CEMENT

The specific gravity of Portland cement dried by heating up to 120° C. should not be less than 3.05.

The specific gravity is determined by means of Le Chatelier-Candlot and Schuman-Michaelis volumeters, the description and use of which is given in the notes. The above instruments are capable of giving accurate indications up to 0.02.

The average of two indications for a Portland cement is considered to be the specific gravity, but these two indications should not differ by more than 0.02.

Note 1.—The Le Chatelier-Candlot instrument consists of a glass vessel containing approximately 120 c.c., the upper part of the said vessel forms a narrow tube of 20 cm. in length. This tube is provided with a globular convex part which is determined on the lower and upper part by two lines; the volume between the lines is equal to 20 c.c. Above the globular part of the tube are made divisions of 10 c.c. each.

In order to determine the specific gravity of cement, the following instructions should be observed.

(1) The instrument is filled up to the lower line with benzine, and after weighing 64 to 65 gr. of cement to an approximation of one cg., the latter is put into the vessel, by means of a funnel, taking care that no bubbles should be formed.

(2) When the level of the benzine begins to approach the line over the convex part, the cement should be let in with great care. The cement is let in until the level of the benzine reaches one of the divisions between 0 cm. and 2 cm. The cement which is left is weighed, and the weight obtained is deducted from the weight first taken. The difference will show the weight of the cement which has displaced 20 c.c. plus a certain number of tenths of a c.c. shown by the division of the upper part of the tube. By dividing the weight of the cement by volume displaced, we obtain the specific gravity of the cement.

(3) During all the time the operation is in progress, the instrument should be kept in water, except, however, its upper part, but the liquid in the instrument should be lower than the level of the water in the outer vessel.

When carrying out tests it is necessary to observe the following:-

(1) Special attention must be paid to the cement being in a loose state. The samples must be passed through a sieve with 900 meshes to the sq. cm., any air-set pieces remaining must be well rubbed up and passed through the sieves and then mixed with the general bulk of the material.

(2) The liquid must be either benzine or some other liquid which does not affect cement, as, for instance, turpentine oil.

(3) The temperature during the test must not vary and not exceed 15° C.

IV. SETTING CONDITIONS OF PORTLAND CEMENT

(a) Portland cement should set slowly: the initial set should not take place before twenty minutes have elapsed, reckoning from the moment of adding water to the cement, and the final setting should not be less than one hour nor more than twelve hours. The water added to the cement for the purpose of this test should be fresh. The paste of neat Portland cement used for determining both the initial and final setting should be of standard consistency.

(b) The amount of water for standard consistency of the paste of neat cement is determined by the consistency-meter, an instrument consisting of a bar of a diameter of 1 cm. with a plate, the plate and bar weighing 300 gr., the mould being a conical ring 4 cm. in height, its lower diameter being 8 cm. and the upper diameter 9 cm., the cement paste being put into the said ring, while there is also provided a scale with mm. divisions fitted with an indicator.

In order to determine the standard consistency of the paste of neat Portland cement, 400 gr. of Portland cement are gauged with water to form a rather thick paste; the paste is stirred very thoroughly for five minutes, and after it is put, without shaking it as far as possible, into the conical ring placed on a non-absorbing base (for instance, glass), the excess of paste is shaved off. Then the bar of the consistency-meter is carefully lowered so that the indicator should come against division

40 of the scale, after which the bar is allowed to penetrate freely into the paste. The amount of water in percentage to the weight of the Portland cement taken for mixing in respect of which the penetration of the bar corresponds to the position of the indicator against the division 6 on the scale, within the limits of $5\frac{1}{2}$ and $6\frac{1}{2}$, is the standard amount of water to be added for a paste of pure Portland cement.

This quantity of water is determined with an approximation of $\frac{1}{2}$ %.

Note.—The amount of water corresponding to standard consistency of the neat cement paste, for various Portland cements, varies generally within the limits of 22 to 30 %, but in respect of different lots of Portland cement from one and the same factory in a definite supply, it is fairly constant.

(c) In order to determine the commencement of the setting of Portland cement, paste is mixed with the above-mentioned standard quantity of water, and is put as mentioned above in the same manner into the conical ring. Then the cement paste is placed under a needle of circular section of 1 sq. mm. (standard Vicat needle) loaded with 300 gr., which in intervals of five or more minutes is allowed to penetrate freely into the cement paste, a new portion of the paste being each time brought under the needle. The commencement of the setting takes place when the needle, after penetrating into the cement paste, shows on the scale a position corresponding to any division between 0 and 1—viz., for instance, does not penetrate through the paste any lower than a distance of $\frac{1}{2}$ mm. from the surface of the glass plate upon which the conical ring containing the cement paste is resting; and the finish of the setting is determined when the needle does not penetrate into the surface of the paste by more than $\frac{1}{2}$ mm.

In order to determine in a preliminary way the setting time of Portland cement, use can be made of a pat of pure Portland-cement paste with a quantity of water corresponding to standard consistency, prepared on a smooth thick glass plate, in connection with which the pat is made of a diameter of 8 to 10 cm., and of a thickness of about 1 cm. in the middle.

The setting of the Portland cement can be considered as having taken place if a slight pressure with the finger-nail on the pat does not leave any trace on the paste, and if when slightly rubbing the surface of the pat no water appears on it.

(d) The sample of paste of neat Portland cement prepared as

a pat can also be used for the determination of the approximate setting time, in the case of consecutive supplies of Portland cement from one and the same factory. In that case, the setting time is determined by not less than two pats.

*V. CONDITIONS OF CONSTANCY OF VOLUME

(a) A paste of standard consistency of neat Portland cement should preserve its constancy of volume, both in the air and water—viz. pats prepared with a paste as shown in paragraph 4, when tested by heating and in water (for twenty-seven days), must neither show any signs of distortion or edge fractures. Not less than two pats shall be used of each kind for the testing of the constancy of volume.

(b) For testing by heating, the pats, twenty-four hours after mixing the paste, and in any case never before the expiration of the setting time of the Portland cement, are placed in an air bath, where they should remain not less than an hour and at a temperature of 120°C . The cracks which appear, not on the edges of the pats but in their centre, as concentric surface hair lines, not to be considered as signs of any alteration in the volume of the cement paste.

(c) For testing in water, pats are placed in water twenty-four hours after mixing the paste, where they are allowed to remain for twenty-seven days.

Note.—Pats prepared specially for slow-setting cement should be sheltered from draughts, also from the action of sun rays up to the time of setting (completion of the setting time). This is easily achieved by placing them in closed boxes or by covering them with a wet cloth. In this manner, cracks due to drying are avoided, the same being generally formed in the middle of the pats, and they might be mistaken for cracks caused by inconstancy of volume.

If the Portland cement tested, seven days after mixing the paste, complies with the specifications stated in paragraph 7 as regards tensile strength (when it is allowed to dispense with the tensile-strength tests twenty-eight days after mixing the paste), the test during twenty-seven days in water—besides the heating test—shall not be required for accepting the cement, but it should nevertheless be made for the purpose of checking the results of the heating test. Should the checking test in water during twenty-seven days reveal any inconstancy of volume in

the Portland cement, then the acceptance of following supplies of Portland cement from the same factory shall take place only on the basis of the results obtained with the test under water for twenty-seven days.

VI. FINENESS OF GRINDING OF PORTLAND CEMENT

Portland cement should be ground as fine as possible. When sifting the dried cement through two cement sieves of a size mentioned below, the quantity passing through a sieve of 4,900 meshes to a sq. cm. should not be less than 50 % of the whole quantity by weight of the Portland cement taken for sifting, and the residue retained on a sieve with 900 meshes to the sq. cm. should not be more than 10 % of the whole quantity.

The gauge of the wire used for the sieves should be 0.05 mm. for the sieve with 4,900 meshes to the sq. cm., and 0.1 mm. for a sieve of 900 meshes to the sq. cm. The quantity of cement taken for the purpose of determining the fineness is 100 gr. (the weighing should be done with an approximation of 0.1 gr.).

VII

(a) *Conditions of Testing Portland Cement in Respect to Tensile Strength*

The mechanical strength of Portland cement is determined by testing it for tensile strength, the test samples being composed of a paste of neat cement and a mixture of cement with addition of sand. All tensile tests of Portland cement are to be carried out by using the same apparatus, also with briquettes of the same section—i. e. 5 sq. cm. at the point of rupture—all samples having been prepared in the same manner.

When preparing the test samples, the quantity of water taken should correspond to that required for obtaining the standard consistency of the mixture, as determined in the provisions of paragraph 4 (b) in respect of neat cement paste, and for mixing a mortar of Portland cement with sand, as shown below in note 1.

In order to prepare the briquettes, the mixture with a large surplus is put into metal moulds which have been cleaned previously and oiled, the moulds being placed upon a base not absorbing water. The briquettes are not to be taken out of the moulds before the mixture has set completely, excepting when they are taken out of the moulds by means of a special apparatus,

in which case they may be taken out as soon as they have been prepared.

The briquettes, both of neat cement paste or cement mortar (*i. e.* Portland cement with addition of sand), should remain during the first twenty-four hours in the open in a damp place, after which they are placed in water, where they remain up to the moment of being tested. The water into which the samples are kept must be changed once a week.

Note 1.—Determination of the quantity of water to be added to obtain a standard consistency of the standard mortar made with Portland cement and sand.

The quantity of water to be added to the dry mixture of one part of Portland cement to three parts of standard sand, in order to obtain a standard consistency of standard mortar (*i. e.* with sand) is determined either by a certain mechanical action exercised by a "cement ram," or accepted according to the information afforded by the factory. If the quantity of water cannot be determined with the help of a "cement ram," and is not indicated by the manufacturer, it is necessary to take 10 % of water of the weight of the dry mixture, and alter the said quantity according to what is really required to obtain a mortar which can be conveniently worked.

In order to determine with the help of the "cement ram" test, the quantity of water to be used to obtain the standard mixture in question, to 750 gr. of dry mixture consisting of one part of Portland cement to three parts of standard sand, there is added such a quantity of water as may be required so as to obtain a rather damp mortar.

The mortar having been worked through is placed into a mould and pressed by means of mechanical strokes of the "cement ram," at the rate of one kilo to every 10 gr. of dry mixture, after which, should the mortar be of standard consistency, some liquid should be coming out from underneath the mould.

Note 2.—For the preparation of briquettes of neat Portland cement paste.

Before cutting off the surplus of the paste contained in the moulds the plates on which the latter are placed should be lifted on one side and knocked slightly against the table. Slightly damp blotting-paper is to be placed between the moulds and the plates.

Note 3.—For preparing a mixture of Portland cement and sand (standard mortar).

The standard mortar is forced into the mould by hand with a trowel, weighing up to 250 gr., or with a wooden hammer of the same weight or with a ram apparatus; until there appears water on the surface of the mortar. Then the surplus of mortar is cut off and the surface is made even with a knife. No addition or any second forcing in of the mortar into the mould is allowed.

(b) *Testing the Samples of Neat Portland Cement Paste*

The testing of the briquettes is carried out on the Michaelis apparatus, six samples being tested at the same time, and the average strength of the Portland cement tested is to be determined by the average of the four highest figures of strength shown by the tests.

Before carrying out the tests, any irregularities appearing on the briquette after it has been taken out of the water are smoothed off, taking, however, great care not to injure the briquette. The load is applied mechanically and at a regular speed—for instance, about 7,500 gr. per second.

The samples of paste prepared from neat Portland cement must have within seven days of being gauged a strength of not less than 20 kilos, and after twenty-eight days of not less than 25 kilos per sq. cm.

If within seven days of being mixed, Portland cement should have a strength of not less than 23 kilos per sq. cm., the tensile-strength test after twenty-eight days of being gauged is not required for the acceptance of the cement, but it should nevertheless be carried out for the purpose of checking the results of the seven days' test.

If when carrying out the checking tests after twenty-eight days from the time of gauging, the strength should be found to be less than 25 kilos to 1 sq. cm., any further supplies from the same factory shall be accepted only upon the basis of the results of the tests carried out twenty-eight days after gauging.

(c) *Testing Samples of Mortar Consisting of a Mixture of Portland Cement and Standard Sand*

In order to prepare briquettes for the above-mentioned test the mixture is made of one part of Portland cement to three parts of standard sand by weight. The sand used for the purpose should be quartz, washed, sifted through three sieves of 64, 144 and 225 meshes to the sq. cm. The residue obtained

by sifting through the sieves of 144 and 225 meshes, mixed together equally, shall constitute standard sand. The gauge of the wire used for the sand sieves should be 0.4 mm. for the 64-mesh sieve, 0.3 mm. for the 144-mesh sieve, and 0.2 mm. for the 225-mesh sieve. The briquettes prepared in the way indicated with a mixture of Portland cement and standard sand, should have a tensile strength, seven days after gauging the mortar, of not less than 7 kilos per sq. cm., and twenty-eight days after gauging the mortar, of not less than 10 kilos per sq. cm. If the mortar of Portland cement and sand, seven days after gauging the mortar, should have a tensile strength of not less than 8 kilos to the sq. cm., and should the Portland cement at the same time satisfy all the requirements as provided by paragraphs 3 to 7, the cement may be accepted without it being necessary to test the same after twenty-eight days, but the test after twenty-eight days should nevertheless be made in order to check the results of the seven days' test.

Should the tensile strength of the cement and sand mortar, on being tested after twenty-eight days, be less than 10 kilos per sq. cm., the further supplies of Portland cement from the same factory shall only be accepted on the basis of the results of the tests made twenty-eight days after mixing the mortar.

General Remark to Paragraph 7.—In case of supplies wanted for urgent work, the Portland cement from known firms may be accepted before the seven days' period has expired, but not before the four days, if, after satisfying all the stipulations of paragraphs 3 to 6, the tensile strength thereof, at that period, is not less than 7 kilos to the sq. cm.

VIII. COMPRESSION TEST OF CEMENT MORTAR IN THE PROPORTION OF ONE TO THREE

Tensile strength tests are to be considered the fundamental tests for determining the strength of Portland-cement supplies, but the supplier, upon the request of the purchaser, should undertake to submit the results of official tests, such as will show that the proportion between the compression strength and the tensile strength, respectively, is not less than 8, in the case of his cement, after twenty-eight days.

At the same time, when there are subsequent supplies the purchaser is entitled, at his option, to make with each fifth supply compression tests after twenty-eight days, whereby the

compression strength obtained in the manner described here-above, should not be less than eight times the tensile strength and not less than 100 kilos to the sq. cm.

In case of a high tensile strength, not less than 18 kilos to the sq. cm., it is permissible to lower the proportion between the compression and tensile strengths, respectively, to 7.5.

The samples for compression tests should have the standard measurements of $7 \times 7 \times 7$ cm., and be prepared mechanically, following in every respect the provisions stipulated for the preparations of the samples for determining the standard consistency of mortar 1 to 3 (see paragraph 7, note 1).

The compression strength is calculated by taking the average of the results obtained from three samples, twenty-eight days after preparing, and, in any case, when the results are equal from not less than two samples.

Should the results of the compression tests be unsatisfactory, whilst satisfying in every other respect the present technical stipulations, it is permissible to carry out another compression test in the same way, and should the second test not give satisfactory results, the Portland cement supplied shall be rejected.

IX. PACKING AND WEIGHT OF CASKS

The casks of Portland cement should have a standard weight of $10\frac{1}{4}$ pood of cement net (exclusive of the weight of the casks) and about 11 pood gross. In order to check the weight of the cement supplied, it is sufficient to determine the weight of the casks with the cement (gross weight).

The accounts for cement supplies are made out according to the net weight of the cement, not counting the waste from shaking. The casks should be marked clearly with the words "Portland Cement," and also bear the name of the factory, number of the lot and the year when the Portland cement was prepared.

Portland cement in bags is accepted only by agreement in each separate case, between the party ordering the cement, and the factory supplying the same.

Not more than 2 % waste caused by shaking of the cement is to be allowed, and the determination of the waste allowed for each separate supply in proportion to its quantity is agreed upon between the parties giving the order and the factory which supplies the cement. For waste through shaking above the

normal quantity, a corresponding deduction is to be made when the money for the cement is paid to the supplier, if the delivery had to be made to the place where the work is carried out.

EXTRACTS COVERING THE ESSENTIAL POINTS IN THE NEW ARGENTINE GOVERNMENT CEMENT SPECIFICATION

Chemical Composition.—Article 1. The cement must not contain more than 3 % of magnesia, and it must not contain any free lime. The coefficient of hydraulicity must not be less than 2.44.

As regards the sulphuric anhydride, the cements will be divided into two categories, as follows—

Category A must not contain more than 1.2 % of sulphuric anhydride. This will be employed in all works in contact with salt water, in all works of the Health Department, and in those where it may be stipulated in the corresponding specification.

Category B: for works in general the amount of sulphuric anhydride contained in the cement must not exceed 2.4 %.

Conditions of Acceptance.—Article 2. No tender will be accepted for the provision of cement destined for national works unless it is shown that the cement comes from manufactories which have already proved sufficiently the good and constant quality of their products.

Every shipment of cement must be accompanied by certificates of its origin, and showing that it fulfils all the stipulations specified, not only as regards its chemical composition, but also as to its strength, fineness of grinding, etc. The certificates of origin will be viséd by the corresponding Argentine Consul, and the other certificates must be issued by the laboratories or test offices belonging to the Ministry or Department of Public Works in the country where the cement is manufactured. Notwithstanding this test, the director of the works in which the cement is to be employed will have the tests and analysis repeated when he may think necessary.

Sampling.—Article 4. This provides that five samples shall be taken from every shipment, or a larger number if the director of the works should think it necessary. The cement will be

taken from the periphery to the centre of the barrel, and must be intimately mixed, so that the sample corresponds to the entire contents of the barrel, and not to a certain part of it. Each sample will be tested separately, and must be kept until the moment of testing in hermetically closed bottles.

Compliance with Specification.—Article 5. The samples taken will be submitted to the necessary tests, to see whether they satisfy the conditions specified. When three or more of the samples fail to satisfy all the conditions, the parcel will be considered suspicious, in which case further tests will be made on fresh samples. If the new results obtained are the same, the whole parcel will be rejected.

Article 6. The minimum specific gravity in the manufactory will be 3.10, and on delivery at the works 3.05.

Article 7. The cement must not leave more than 2 % residue on a sieve of 900 meshes per square cm. The residue on a sieve of 4,900 meshes must not exceed 20 %. The wire of the first sieve will be of 0.15 mm., and of the second 0.05 mm. One hundred gr. of cement will be employed for the tests. This cement will be successively sifted in the sieves mentioned. The operation will be done by hand, and will be considered finished when not more than 0.1 gr. of cement passes through the sieve at the end of twenty-four shakes of the arm. The residue will be calculated by adding to that which remains on the sieve of 4,900 meshes that which remained on the sieve of 900 meshes.

Rise of Temperature on Gauging.—Article 8. On gauging the cement to its normal consistency, the temperature of the cement must not rise more than 2° C. In the contrary case, the cement will be declared suspicious.

Water to be Used for Gauging.—Article 9. In the tests in which the employment of water is necessary, the same water must be used as that which the cement will have to be in contact with. The same water must be employed for mixing the cement, and for storing the briquettes, pats, etc. With the exception of the tests in hot water, the temperature of the water must be maintained between 18° and 20° C.

Normal Consistency.—Article 10. All tests on neat Portland cement are made with the cement gauged to normal consistencies. This is determined by means of the Tetmejer apparatus.

Setting Time.—Article 11. The setting time of cement reduced to a paste of normal consistency must not develop initial set

in less than thirty-five minutes. The final set shall not take place in less than three hours, nor more than eight hours, calculated from the moment the water was added to the cement—that is, when fresh water is employed. When sea water is used, the limits mentioned above will be two hours, six hours, and twelve hours respectively.

When circumstances make it necessary to modify the periods of time at which the initial and final set takes place, this will be established in the respective contract.

The setting will be determined by the use of the Vicat needle under the usual conditions.

Tensile Tests Neat.—Article 12. From each sample of cement twelve briquettes will be made in two lots of six. Three of each series will be broken at seven days (one day in the air and six in the water), and the other three at twenty-eight days.

The briquettes will be broken in the Michaelis machine, the fall of the lead shot being graduated at the rate of 100 gr. per second. The tensile strength in each test will be the average of the three highest results, and will be expressed in kilos per sq. cm.

The tensile strength determined in this manner shall be not less than 30 kilos per sq. cm. (426.6 lbs. per sq. in.) at seven days, and not less than 35 kilos (497.7 lbs. per sq. in.) at twenty-eight days. In addition, the strength at twenty-eight days must exceed by 5 kilos (71 lbs.) that corresponding to seven days. This condition will not be exacted when the minimum strength at seven days is more than 45 kilos (640 lbs. per sq. in.) per sq. cm., but in no case whatever must the strength at twenty-eight days be inferior to that at seven days.

Tensile Tests (Mortar).—Article 13. The quantity of water to be added to a kilo of the mixture (1 to 3) of cement and sand will be determined in gr. by means of the following formula—

$$45 + 1/6 P,$$

P being the weight of the water necessary to reduce a kilo of cement to the condition of a paste of normal consistency. The mortar will be filled into the moulds by means of a hammer apparatus, in which a hammer of 2 kilos weight falls on the briquette from a height of 40 cm. The number of blows will be 120.

The minimum tensile strength at seven days shall not be less than 12 kilos (170.6 lbs.) per sq. cm., and that at twenty-eight

days not less than 15 kilos (213.3 lbs.), while it must exceed that at seven days by 2 kilos (28.5 lbs.) at the least.

Constancy of Volume.—Article 14. Pats will be made under the usual conditions. Two of the pats will be kept in cold water in the same conditions as the briquettes for the tensile test. Two pats will be kept in air saturated with moisture and protected from currents of air and direct rays of the sun, at a temperature between 18° and 20° C. In neither case must the pats show any alteration or signs of crack or deformation, no matter how long the observation may be prolonged. Two pats will be submitted to the action of hot water, as follows—

Within twenty-four hours from setting, the water in the vessel containing the pats shall be gradually heated, until at the end of half an hour it starts to boil. This will be prolonged for six hours, and the water will be allowed to cool at once. The pats must show no alteration after this operation.

Briquettes of pure cement of the shape of the figure "8" will be submitted to the action of boiling water in the form indicated above. These will be afterwards kept in water at a temperature of 18° to 20° C., and must not, at the end of the seventh day from having been made, give a less tensile strength than that already obtained in the ordinary tensile tests.

Test-tubes will be filled with cement in a paste of normal consistency. After the setting is complete, none of the tubes must have cracks, nor must the cement detach itself from the sides of the tube.

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